INTERNATIONAL HELLENIC UNIVERSITY

Co-processing of castor oil with fossil-based feedstocks in conventional refinery processes for the production of high quality 2nd generation biofuels

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SCHOOL OF SCIENCE & TECHNOLOGY

A thesis submitted for the degree of

Master of Science (MSc) in Energy Technology Systems

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OCTOBER 2015

THESSALONIKI – GREECE

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Abstract

Energy is one of the most important considerations of modern world. More than half of the energy is consumed in the form of transport fuel. Thus in light of considerations such as global warming, energy security and even economic growth there is significant interest in the development of renewable fuels. These biofuels can be produced from a wide variety of sources but the interest is currently focused on the utilization of sources and processes that maximize production and quality while minimizing strain on environment, land use, food supply etc. Biofuels that meet these requirements are characterized as second generation. A promising biomass source for the production of 2nd generation biodiesel is castor oil which is widely used in the automotive lubricant industry.

For such biodiesel to be viable economically and compatible with current technology the production process needs to be integrable with existing infrastructure and feedstocks, for coproduction and able to produce high quality fuel, free of heteroatoms and with elevated physical qualities. For this purpose, mono and bimetallic bifunctional catalysts made from combinations of Pt, Ir and Pd supported on amorphous silica alumina where evaluated for use in hydrogenation processes on model compounds. Monometallic Pt was deemed to have the greatest potential and was subsequently tested on a feedstock representative of an industrial setting corresponding to the co-processing of Castor oil along with VGO. The catalyst had a beneficial impact on the quality of the product, removing Sulphur and upgrading the product's pour point. Both before and after testing all catalysts where characterized to determine their characteristics and the quantity and quality of coke formation.

The author would like to thank Dr. Eleni Heracleous for her guidance throughout the course of this thesis as well as her understanding and patience especially in the later part. Additionally the author would like to thank Fani Tachoula for a great collaboration throughout the conduct of the experiments and for sharing her experience and insight without which this thesis would not be possible.

Ilias Eleftheriou

11/12/2015

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1 Introduction

In the last two and a half centuries, since the industrial revolution begun to change the world, the population of the planet as well as the standards of living (at least in the developed countries) has risen at rates never before seen and as a consequence, so did energy consumption and the dependency of the world on fossil fuels.

As emerging economies, like the so called BRICS (namely Brazil, Russia, India, China and South Africa), which when put together account for over 3 billion people, require more and more energy to sustain their development, the pressure put on the existing petroleum and natural gas reserves is continuously increasing while the amount of fossil resources is continuously decreasing.

In light of the ever increasing demand for energy and the finite as well as relatively localized nature of the fossil resources, there is a growing, worldwide, concern about the future of energy security and the impact of the eventual depletion of energy sources. Thus a lot of effort, money and scientific research have, for decades, been dedicated to the development of renewable sources of energy.

Currently, renewable resources account for only a small fraction of the energy demand due to the lack of the necessary technologies and the fact that fossil resources remain an economical solution for the time being. Thus renewable energy is generated and consumed, alongside conventionally generated energy, only as a supplementary source.

Indeed fossil fuels account for almost 4/5 of the world primary energy consumption. The larger portion of this energy (about 58%), is consumed in the form of fuel for transportation [1]. The fuels used for that are mainly gasoline, kerosene, heavy oil and diesel but as the interest in renewable energy is increasing, there is an increasing amount of research and interest in the use of biofuels.

1.1 Biofuels - Biorefinery

Biofuels differ, from conventional ones, in terms of feedstock and depending on the method of production, refinement and source they can differ in composition and properties such as viscosity, pour point, energy density and others.

The feedstock for producing biofuels is, instead of petroleum, biomass. By biomass we refer to organic matter that can be available to us in many forms, such as agricultural, municipal, urban and industrial waste, residues from farming activities and husbandry, dedicated energy crops, aquatic plant life and even sewage [2]. By utilizing all this biomass we can create a variety of fuels of different properties and usages [3], the most important of which, as far as transportation is concerned, are bioethanol and biodiesel, through various processes an overview of which can be seen in Figure 1.

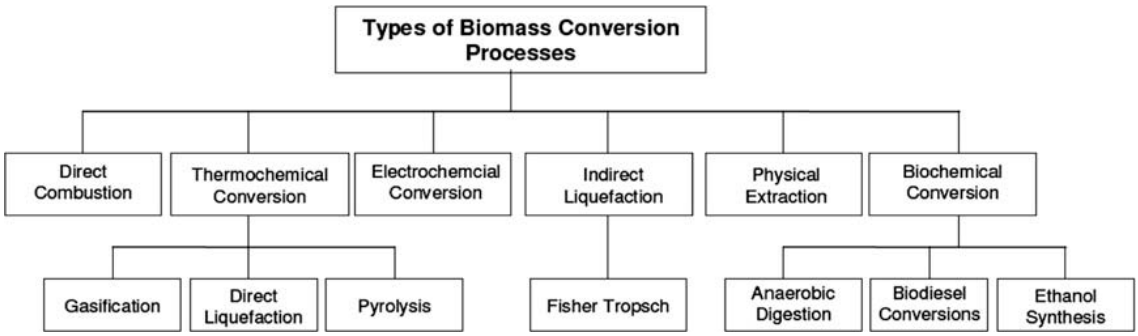


Figure 1 Overview of biomass conversion processes [4]

Converting biomass to biofuels and using them alongside the existing fossil fuels can be complicated because the multiplicity of the biomass sources and their differing natures, results in a resource of varying characteristics and qualities. Furthermore biomass, in contrast to petrol, is not conveniently situated in large reservoirs that we can discover and develop; although this can also be an advantage in more than one ways.

Instead it is a dispersed resource that needs to be collected through various means, depending on the form it comes in. The collection and transportation of the biomass can pose economical, technical and even health issues (i.e. in the case of sewage) that may or may not be common to petroleum; as in the case of sewage or manure where measures have to be taken to protect personnel against pathogens that may be present.

Despite the difficulties posed by the nature of the raw material, biofuels constitute a subject of continuous research and innovation.

1.1.1 Why biofuels

This interest in biofuels is a result of the increasing attention given to alternative energy sources and the lack of appropriate energy carriers needed for the proliferation of renewable energy. The driving factors behind their development are:

- Technical compatibility
- Environmental concerns
- Energy security and independence
- Rural development

The ever increasing concern about the environmental consequences of the extended use of petroleum products in all facets of our everyday life, from plastic products to fuels to electricity, has placed alternative sources of energy, like solar radiation and wind power, under constant investigation and continuous scientific research.

One of the difficulties impeding the wide adoption of these energy sources is the fact that the energy generated is not available constantly but intermittently. Indeed renewable energy production is subject to weather conditions, the circle of night and day and even seasonal differences. Thus efficient and cheap storage of the energy generated is of paramount importance to make renewable resources a viable alternative to fossil resources. This has been achieved until now through the storage of water in reservoirs for the production of hydroelectric power. Unfortunately appropriate locations for the creation of such reservoirs are limited and the creation of new reservoirs can have serious environmental and social repercussions such as loss of biodiversity and habitat as well as the displacement of large populations (i.e. the case of the Three Gorges Dam). Thus practical storage of the excess energy is at best very difficult if not impossible with the limitations of our current technological level.

Even if practical storage of renewable energy was available its effect would be progressive, as, especially, in the case of transportation there already exists a huge infrastructure, in the form of fuel production, transportation and distribution and internal combustion engine technology, which is unlikely to be phased out and replaced in the foreseeable future.

The issue of energy storage and integration into existing transportation technologies is what gives biofuels a competitive advantage against other forms of alternative energy sources.

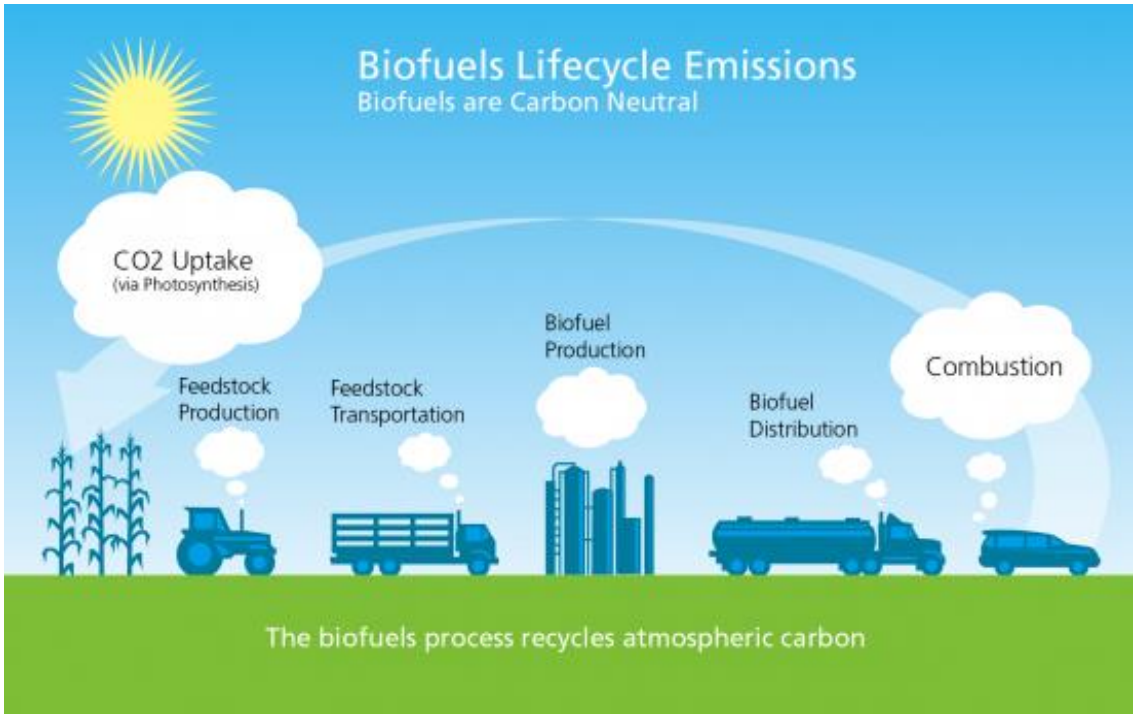
As far as energy storage is concerned the adoption of biofuels does not require any exotic or novel technologies as they themselves are the carriers of solar energy since they are derived from biomass which is the product of photosynthesis. Furthermore since their properties do not radically differ from that of fossil fuels and in any case they can be made quite similar with the appropriate processing, most storage facilities and technologies used for conventional fuels can be used to store biofuels with little to no modification.

As far as the existing infrastructure is concerned biofuels can, as in the case of storage, be used as fuel for existing vehicles with little to no modification required to the current technology, either alone or in mixtures with fossil-derived fuels [5] provided they undergo appropriate processing to improve their properties.

Compatibility with current technology is a major advantage for the adoption of biofuels but the reason they can be of value in tackling the worldwide problem of climate change is their potential for carbon neutrality.

Biofuels, as was mentioned before, are derived from various types of biomass. That in itself is enough to make them appealing since, at the very least, their inclusion into our fuel mix gives usefulness to raw materials that would otherwise be discarded as waste. The use of biomass as feedstock for the production of fuels, results, indirectly, in the emission of less carbon dioxide since its use reduces the need for fossil fuels while the emitted greenhouse gases would be have been emitted anyway through the natural decomposition of the biomass.

The carbon neutrality potential of biofuels is a result of the fact that the biomass that is converted to fuel is continuously replaced by new growing biomass. If the whole process is well planned and executed the carbon oxide emissions, resulting from the production and consumption of biofuels, end up being absorbed by the growing biomass to be used again for the production of fuel so the circle is complete and we have continuous recycling [6]. This is known as a carbon neutral circle, which is overviewed in Picture 1. This of course is only possible when there is appropriate planning and the biomass used is indeed waste or is actively replenished.



Picture 1: Overview of the biofuel lifecycle

Minimization of the energy demands for the conversion of the biomass, as well as the transportation of the feedstock and the distribution of the fuel products (through technologic or logistic optimizations) is of great importance in order to maximize the energy that is actually available to do useful work and make sure that the energy put into the whole process is not more than what is available at the end. In fact in well thought out and executed scenarios the result might even be a permanent sequestration of carbon dioxide from the atmosphere. The byproducts of the fuel production can be used to displace chemicals like fertilizers that would otherwise have to be produced from fossil resources and potentially transported great distances adding to the energy demand. In such a case the minimization of energetic demand and the optimum utilization of all the byproducts can lead to a more efficient utilization of energy; thus in the long term the move from traditional resource utilization to novel ones that make use of biomass can lead to permanent carbon sequestration since less energy is needed for the same activities.

The minimization of the energetic demand of the conversion of biomass depends on technological advancements, while the reduction of transportation and distribution demands is also a matter of logistics. The efficiency of the process is enhanced when the local nature of the resource is coupled with local processing and distribution. In light of this, the dispersed character of the resource can be an advantage as well as a disad-

vantage at the same time. The need to collect the biomass from many different dispersed sources results in much more complicated logistics and is at odds with the current organization of the fuel production and distribution chain, but if the logistics are worked out, it can be a source of economic development for rural areas through the cultivation of land that might not be suitable for traditional agricultural activities [7]. The switch to agricultural activities related to the production of biofuels might stand to be a more profitable occupation in some areas than the traditional ones and the construction and operation of the facilities needed, themselves, can create jobs and invigorate otherwise underdeveloped areas.

This dispersion can also be advantageous in ways that do not have technical or logistical significance. The energy mix (the composition of the energy sources exploited to provide for the energy needs) of a country is a very important issue with consequences in the policy adopted from governments.

This is because it affects the energy security of a country, meaning the ability of the country to meet its energy needs regardless of the international or regional circumstances. It is believed that in order to maximize energy security, it is important for countries and regions to diversify their fuel mix by using as many different energy sources and suppliers as possible and by including renewable energy in the mix so that dependency on any, one, source is low and problems in the supply of energy can more easily be evaded [8] [9].

The dispersed nature of the resource and the conversion facilities can make its denial very difficult and the local character of the raw material makes the country less vulnerable and depended on importing energy and all the complications this might entail. The importance of this fact is more obvious if one considers that the majority of the fossil reserves is under the control of a handful of countries and is routinely used as leverage to further economical and geopolitical purposes. Thus there is interest from political entities like the European Union to push for the adoption of biofuels to, among other things, enhance their energy security [10].

1.1.2 The biorefinery concept – Co-processing

Currently, the facilities needed for the production of fuels, like refineries and transportation and distribution networks, are built and organized in the best way to accommodate the current regime which is the exploitation of petroleum that is extracted from the earth.

Due to its properties as well as the fact that the current infrastructure represents more than a century of investments on the exploitation of petrol, it is relatively easy and cost effective to move petroleum even over great distances and process it in big centralized installations. This is not usually practical or even possible with biomass. In order to make the adoption of biomass easier and more competitive in terms of cost it has been proposed [11] that biomass inlets could be incorporated in existing oil refineries in order to co-process it along with traditional feeds, as shown in Figure 2

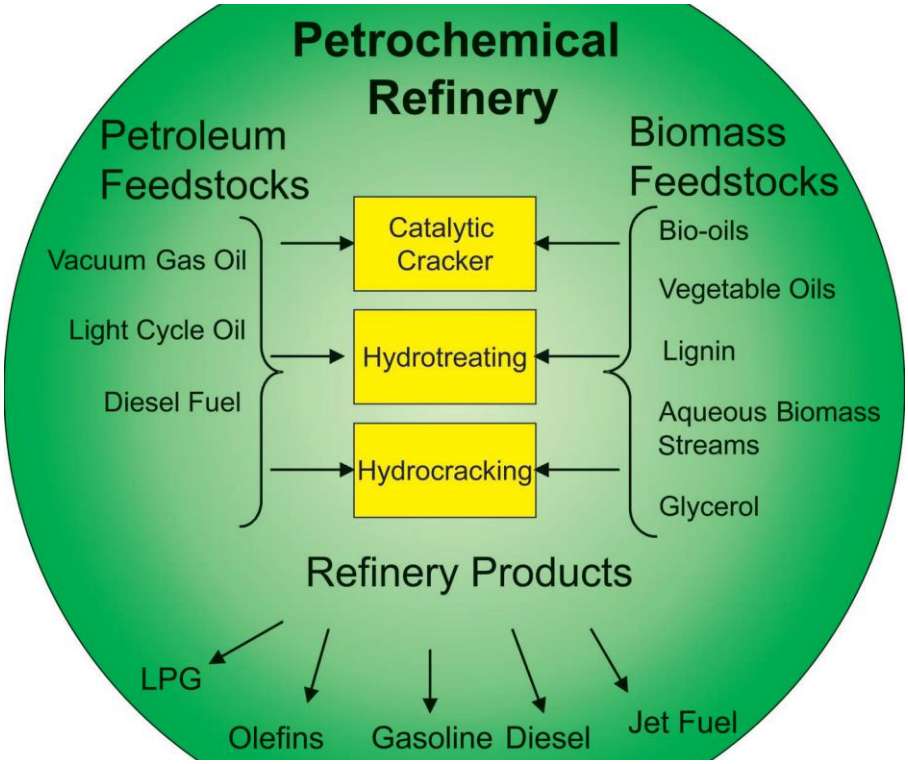


Figure 2:Co-processing of renewable and fossil feedstocks in refineries [12]

This has the advantage of utilizing existing assets, thus greatly reducing the upfront costs of utilizing biomass for fuel production, like building new facilities dedicated to biomass conversion. In an existing refinery renewable feedstocks can be incorporated in the feedstock of Fluid Catalytic Cracking processes (FCC) and hydrotreating/cracking processes. In both cases the resulting fuel is richer hydrogen than its precursor [12].

Nevertheless as biofuels become more and more important in our fuel mix it is more economical, practical and sensible (as far as carbon emissions and sustainability are concerned) to process the resources locally in decentralized facilities and then distribute the products in the local market so as to minimize the logistic, investment and energy requirements, as was described before.

This is where the concept of the biorefinery comes into play. A biorefinery, in its most advanced form, is analogous to a regular refinery where instead of petroleum, the feedstock, is biomass [4]. As in regular refineries, a wide range of different products can be produced, from fuel to materials to power, to even food for human consumption like in-vitro meat [13]; although the primary objective is the production of biofuels.

As a matter of fact, due to the variability of the characteristics of the possible feedstocks, a biorefinery can potentially be able to produce a wider range of products than what is possible for a conventional refinery that can only process petroleum albeit at the cost of more complex design and elevated investment costs [14].

Regular refineries represent very large centralized facilities that incorporate a great number of processes under the same roof in order to drive cost down and maximize technical and logistical efficiency.

This is not necessarily true for biorefineries because of the different logistics involved. While the concept of a centralized facility may be appropriate in many cases it has also been proposed that it is possible that decentralized industrial complexes, the constituents of which can be of various sizes and levels of sophistication and are situated in a way so as to maximize logistical efficiency [7], could be preferable depending on the particularities of every project.

The rationale is that this kind of setup could introduce logistical optimizations that could offset the technical ones addressed in regular centralized facilities, since the dispersed nature as well as the varying transportation needs of the different feedstocks, that can be more cost, energy and labor intensive than that of petroleum, might make an appropriately dispersed facility preferable.

Biorefineries come in three broad categories in order of increasing number of feedstocks and products as well as sophistication [14]:

1. Biorefineries that can accept only one kind of input biomass and convert it into a product
2. Biorefineries that can accept only one kind of input biomass but can give more than one products
3. Finally biorefineries that are sophisticated enough to accept a wide range of feedstocks and turn them to a wide range of products (as regular refineries do)

Of course in terms of investment cost and complexity the third category is the most difficult to build and maintain but this kind of refinery has the highest potential to make the dispersed model of conversion feasible. Such an installation is able to accept whatever feedstock is available at the region where it is located at any given time. Thus it is able to function continuously in contrast to the simpler ones, which are easier to design and maintain but are strongly affected by feedstock availability, which might be intermitted like in the case of energy crops. Given correct design and implementation a biorefinery of this type should produce no waste [15] and ideally require no external energy supply [7].

1.1.3 Governmental intervention, policy and regulations

Even though, for the reasons described above, the adoption of biofuels is desirable and compared to other alternative sources of energy, a relatively easy task; it is not something that can be left to the markets to take care of [16], since at least with current practices, technologies and international circumstances, biofuels are not competitive enough [17] As long as petroleum products remain cost competitive the motivation for the development and production of biofuels cannot be profit driven but will stem from concerns about the environmental and social benefit they can have.

In order to alleviate this lack of competitiveness governments have established laws, regulations and other legal provisions [18] [19] like the European Union's Directive 2003/30/EC, the Renewable Energy Directive (RED) (Directive 2009/28/EC) [20] and its international analog, the United Nations Framework Convention on Climate Change (UNFCCC) as well as international treaties like the Kyoto Protocol; by which they have set goals to be met within specific time frames as well as incentives to invigorate the activities and interest on the matter.

The European Union has set the goal of covering 20% of its total energy needs through the use of renewable energy, reducing greenhouse gas emissions by 20% and reducing its overall energy consumption by 20%, by 2020 as well as heaving at least 10% of the transport fuels come from renewable resources.

Biofuel adoption is very important if the goals set are to be achieved since the transport sector accounts for 30% of the European Union's energy consumption 98% of which is met through the consumption of, mainly imported, fossil fuels [10].

Invigorating commercial and research activities on that direction, is thus important and has been approached in various different ways throughout the Union's member states depending on each markets particularities.

The most followed strategies, among member states, have been giving incentives through tax reduction or exemptions for producing and incorporating biofuels in the fuel mix and obligatory inclusion of some percentage of biofuels in the fuel mix of suppliers. In the past member states have chosen different routes but most have since incorporated both strategies [10] to alleviate their individual shortcomings.

The tax reduction/exemption scheme can be effective but results in revenue drops for the state. Alternatively it can take the form of an increase of taxation on fossil fuels which, in conjunction with tax reduction/exemption on renewables, can counter act the drop in revenue.

Requiring the mandatory blending of some percentage of biofuels in the fuel mix can be a more forceful but effective way of promoting biofuel adoption but has the advantage of providing a more stable and predictable environment for biofuel suppliers to develop their operations since in this way demand for their product depends on the total fuel demand and can more easily be forecasted [10].

Unfortunately the perceived environmental and social benefits of the production and use of biofuels can be insubstantial when their production is left to take place without supervision and appropriate legislation and enforcement.

This is because, as was described before, in order for the biofuels to be carbon neutral, the production process, logistics and methods used have to be well thought out and implemented. If this is not the case the biofuel produced might be even more harmful than regular fossil fuels. Since there is interest in the consumption of biofuels there is also incentive to produce them regardless of the actual environmental value, in order to benefit from the promotion measures taken by governments.

Thus the production methods and practices exercised may be targeted at creating the maximum amount of product in the minimum amount of time and cost; without taking into consideration the sustainability of the process or any other environmental or social repercussions. Furthermore suppliers may choose to import the biofuel from other countries that are not bound by European regulations.

This is undesirable because it is at odds with the development of biofuel production in the member states and does not agree with the purpose of enhancing energy security. Additionally this practice may mean that the biofuels included in the energy mix are no better than ordinary fossil fuels, since the manner of their production cannot be, as easily, verified and may not provide the expected benefits to the protection of the environment. Indeed, in 2008 about 25% of the biofuel demand in the European Union member states was satisfied through imports [10].

The necessity to discourage producers and suppliers from resorting to such practices has been recognized by law makers. In order to ensure that the adoption of biofuels does not inadvertently lead to more damage done to the environment than using fossil fuels regulators have established the, so called, sustainability standards. These sustainability standards are essentially a set of criteria that has to be met throughout the lifecycle of biofuels from cultivation of biomass to consumption of the fuel. In these criteria there are provisions for every facet of biofuel production, distribution and consumption, from land use to production practices, to distribution method [18].

The rationale is that, since the production and distribution of biofuels can be conducted in many ways that may or may not lead to the satisfaction of the intended purpose of their adoption; there need to be guidelines and quality requirements that make sure that best practices are followed by all parties involved.

This along with the fact that the European Union constitutes a major market, inevitably leads to the criteria being imposed to countries and businesses that are not part of the Union but have trade relations with member states [18].

An example of such criteria is that currently the total burden to the environment in terms of CO2 equivalent emissions from the whole lifecycle of the biofuel should not be more than 65% that of regular fuel. This figure will change to 50% by 2016 and to 40% by 80% [18].

In order to operate in the area of biofuels, involved parties need to be able to prove their compliance with requirements and methodological constrains imposed by the European regulations by producing [18]:

- a standard of independent auditing
- "chain of custody" calculations based on mass balance systems

This extends to providing information of the farming practices followed, by the producers, when the raw material for the production of the biofuel is imported.

In order for the adoption of biofuels to become wider and more profitable as well as for political reasons, there is need for larger production capacities. These if achieved can make biofuels more competitive but for this to happen there is need for energy dense sources

1.1.4 1st vs 2nd generation biofuels

For the reasons described above, in countries like Brazil [21] [22] there is a lot of activity and research around dedicating land and workforce in the cultivation of crops, for the purpose of producing biofuels. Overall it is estimated that 2.5% of the land available for crops on the earth is currently utilized for the cultivations of crops to be used for biofuel production.

The biofuels (most importantly bioethanol coming from starch sugar and biodiesel coming from oil rich seeds) that are derived from these crops have come to be classified as 1st, 2nd and in the future 3rd generation biofuels based on the characteristics of the raw materials and associated conversion technologies used for their production; with each generation eliminating limitations of the previous.

Crops that are cultivated for the purpose of producing biofuels have come to be called energy crops. Essentially they act as collectors and storing devices of solar energy and are cultivated for the production of fuel, even though there may be byproducts that can be used otherwise.

First generation biodiesel is produced mainly from oils coming from rapeseeds, soybeans, palms and coconuts, while bioethanol is produced by fermenting crops like sugar cane, cereal, maize and others but most importantly corn.

Such crops can enable intensified production of biofuels, of high quality but at the cost of leading to the use of more farmland, intensified water and fertilizer consumption, greater need for workforce and competition with the food chain [23].

This is because the so called 1st generation biofuels that are, at present, the primarily produced variety, make use of crops that are normally used for the production of food such as corn, soybean and sugar cane; an overview of the main first generation crops by country and yield is presented in Table 1. The farmland required and the plant product can either be used as food or as feedstock for fuel production. The use of commodity crops like sugarcane, corn and wheat for the production of biofuels can lead to elevated food prices and force farmers to intensify their production by following practices that are, in the long run, harmful both to the environment and to food supply security [24]. In places with water or food shortages, finding a balance between the two purposes can be problematic.

Table 1: Most important energy crops by country and yield

Type of biofuel	**Crop**	**Biomass Yield (ton/ha)**	**Biofuel Yield (m^3/ha)**	**Country**
Bioethanol	Corn	9.9	3.8	US
//	Sugarcane	79.5	7.2	Brazil
//	Sugarcane	60	5	S.Africa
//	Sugar beet	79.1	7.9	EU
//	Wheat	5.1	1.7	EU
//	Wheat	4.7	1.7	China
//	Cassava	13.6	0.137	Brazil
Biodiesel	Rapeseed	3.1	1300	EU
//	Soybean	2.8	600	US
//	Oil palm	18.4	4200	S.Asia

In addition the processes used for the production of 1st generation biofuel do not make use of the whole plant but only use parts of it. This results in a large volume of waste plant matter (although it may be possible to make use of the residues in different ways) and inefficient use of fertile land that could be used for other purposes.

The inefficient use of land is a major drawback of 1st generation biofuel sources. As the demand for biofuels grows, producers are driven to extend their production. The additional farmland required for the cultivation of the crops is usually acquired through the deforestation of large areas; threatening biodiversity [25] [9] and when this is not the case there is further displacement of food crops.

Along with the intensification of production and the use of more land, grows the need for more water [26] [27], fertilizers and the dedication of more workforce on the cultivation, harvest and transportation of materials and plant matter.

Furthermore the inefficient use of farmland means that the cultivation of energy crops needs a lot of space and therefor greater energy expenditure in every stage of the cycle from planting to harvest and transportation of the product. This energy requirements and as well as the consequences of deforestation can end up negating any environmental benefits to be had by substituting fossil fuels with biofuels.

The limitations of the crops and technologies used can render the resulting biofuels environmentally unfriendly [28] if the logistics, and the practices used in the cultivation of the crops are not worked out properly.

In any case the resulting energy balance is not as good as it could be and can be offset by, undesirable, side effects. The concerns described above impede the adoption of biofuels and are the reason that bioenergy does not see the development it could around the world [29].

In light of all these, in recent years, the attention of research as well as the focus of the governmental policies have shifted to the so called 2nd generation of biofuels. This second generation has the potential to reduce the effect of the controversies described above. This is because these biofuels require less land, water, fertilizers and workforce to be produced.

This is achieved by utilizing sources that are of no use as food and require little or no fertile land that could be used otherwise. Such sources of biomass can be broadly categorized as waste matter and dedicated energy crops.

Waste matter can take the form of residues that result from forestry and agricultural activity such as leaves, stalks and cobs of plants like corn and straw, manure and poultry waste. In addition, municipal waste as well are waste that result from industrial and economic activities such as food scraps, oils, fibers and a multitude of other residues can be used.

Their utilization is more difficult than that of energy crops (both first and second generation) due to the potential lack of homogeneity of the raw material. Nevertheless it has the advantage of making use of materials that would otherwise have had to be dis-posed of as waste, saturating landfills and burdening the local environment if recycling is not

possible, as well as representing an expense in the form of waste management for the local authorities.

Dedicated energy crops are crops that are chosen on the basis of not having the limitations of the first generation energy crops. The point in case is to derive the fuel from plants that cannot be used as a food source themselves and can grow on land that is not very useful for food crops. In this way, land which is usually considered useless, can be utilized and the fuel production process can have a much lower effect on food production. This can have the added benefit of leading to rural development of marginal lands and can lower the competition with the food chain [30].

In contrast to their 1st generation counterparts, 2nd generation biofuels make use of most, if not all, of the plant so that land use efficiency is maximized and there is much less waste material dispose of as well as smaller energy expenditure required. In addition such crops require less water, fertilizers and care on behalf of the farmers.

Combinations of crops that give harvest at different times of the year or individual crops that can be harvested more than once per year have the potential of minimizing storage requirements and providing greater stability to the operation of the whole conversion chain.

Crops that meet these requirements include perennial grasses and fast growing trees and various seed crops. Of particular interest are plants like Jatropha that are able to grow on lands that are useless for the production of other products [31].

1.2 Vegetable oils for the production of 2nd generation biofuels

Crops for second generation biofuels need to give high yields, in order to maximize land use efficiency, be inedible to avoid conflicts with food production and require as little processing as possible to produce fuel. Certain variables of vegetable oils are a very promising feedstock for the production of second generation biofuels and specifically biodiesel.

Vegetable oils have been used for thousands of years, not only for food, but also for other purposes that are now fulfilled by petroleum products, such as for lubrication and lighting and even as materials in the production of cosmetic products.

In the framework of renewable energy, they are a very good raw material for the production of biodiesel, due to their chemical makeup. Biodiesel is essentially a mixture of

Fatty acid/ethyl methyl esters (FAME/FAEE) that contains hydrocarbon chains in the range of diesel (C_8–C_{25}) and can be used instead of or in mixtures with regular diesel as a fuel. Vegetable oils are a great source for the production of this kind of, diesel range, alkyl esters via the transesterification reaction. An overview of the general process most widely used for the production of biodiesel, currently is presented in Figure 3.

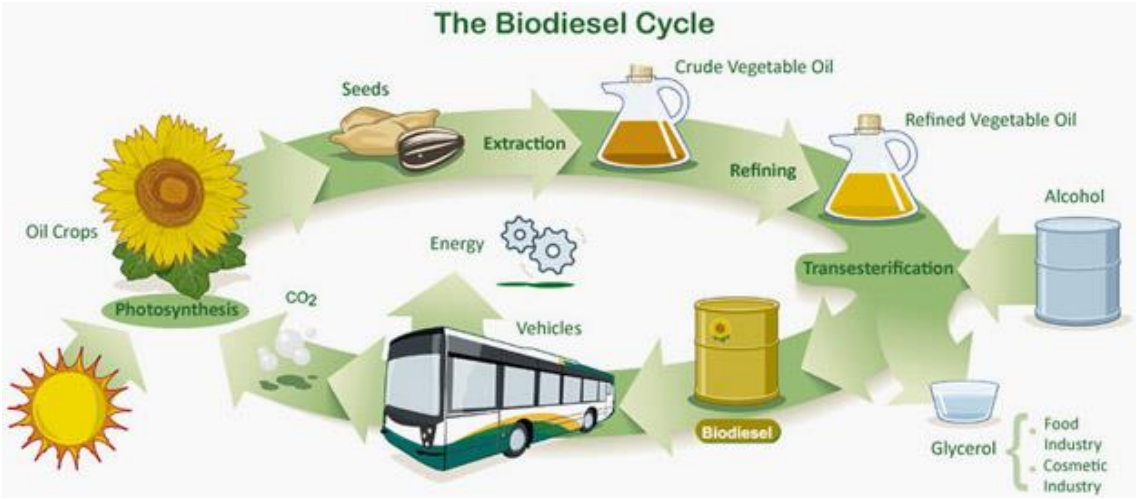


Figure 3: Indicative biodiesel production process

There are more than 350 different crops that can be used in oil extraction processes [12]. The vegetable oils extracted are consisted, mostly of triglycerides (98%) [32] with minor quantities of diglycerides and monoglycerides, made of three, two and one fatty acids (respectively) connected to a glycerol molecule as shown in Figure 4. These fatty acids make vegetable oils useful in producing biodiesel because they contain long chains of hydrocarbons in the range of diesel.

Furthermore they can be used for fuel production even after they have been used for other purposes, like in the case cooking oil, via processes like catalytic cracking and hydrogenation [33]. The incorporation of waste cooking oil (so called yellow grease) and oils that are collected in water treatment facilities (so called trap grease) provides a way to utilize waste material that would otherwise have to be disposed of [12].

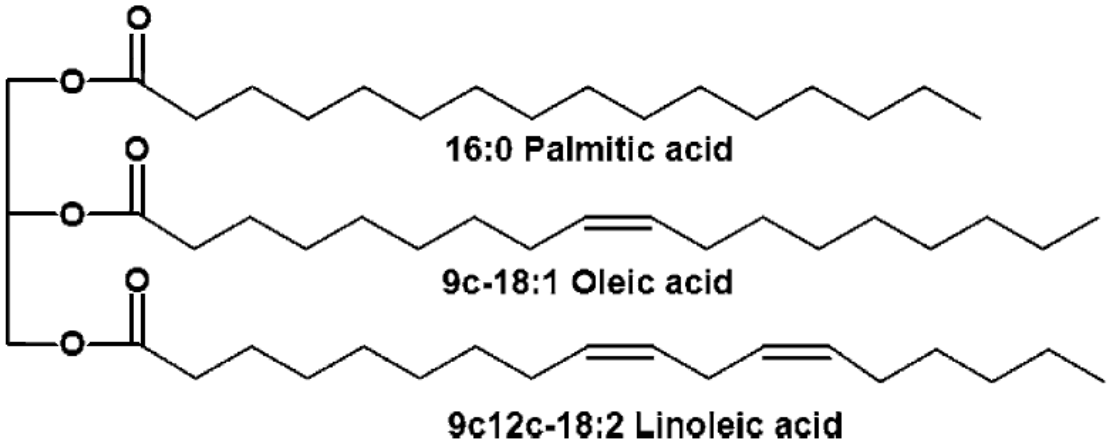


Figure 4: Schematic representation of the structure of a hypothetical triglyceride [34]

The main methods used to upgrade vegetable oils for the production of biodiesel are [35]:

- Microemulsion
- Thermal cracking
- Transesterification

The transesterification process is, currently, the most used method for the purpose of producing biodiesel. The process can take place without a catalyst but catalysis of the reaction is preferred, to boost production. The main methods include homogeneous and heterogeneous catalysis as well as non-catalytic processes, an overview of which is presented in Figure 5.

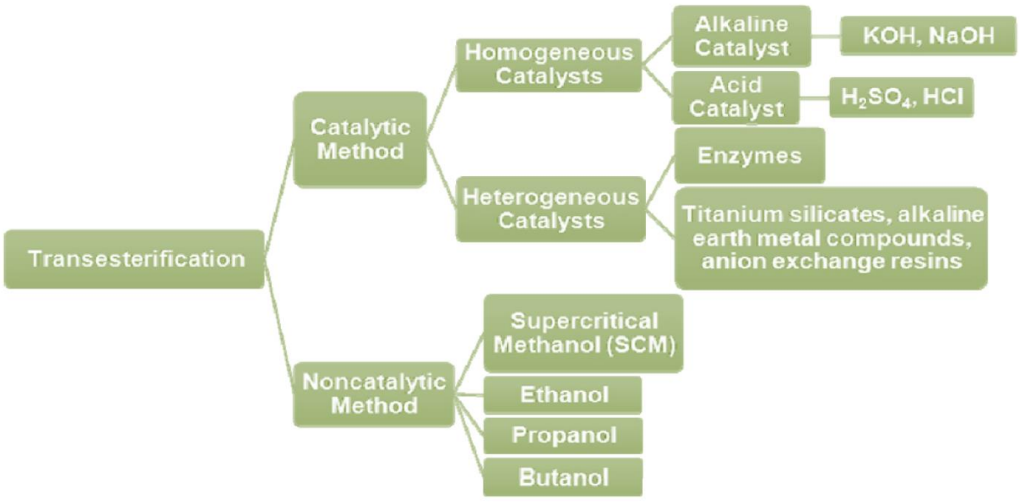


Figure 5: Overview of transesterification technologies [36]

Figure 6 shows the transesterification reaction between the triglycerides and alcohol for the production of fatty acid alkyl esters (FAAE) with glycerol as a by-product. The reaction proceeds in three stages that were omitted from Picture 4 for the sake of brevity.

In the first reaction one molecule of alcohol reacts reversibly with a triglyceride to produce an alkyl ester, a diglyceride and a water molecule. The same reaction happens then between alcohol and the diglyceride and then with the produced monoglycerides. In the end the product is composed of three alkyl esters three water molecules and one glycerol that need to be separated before the esters can be used as a fuel.

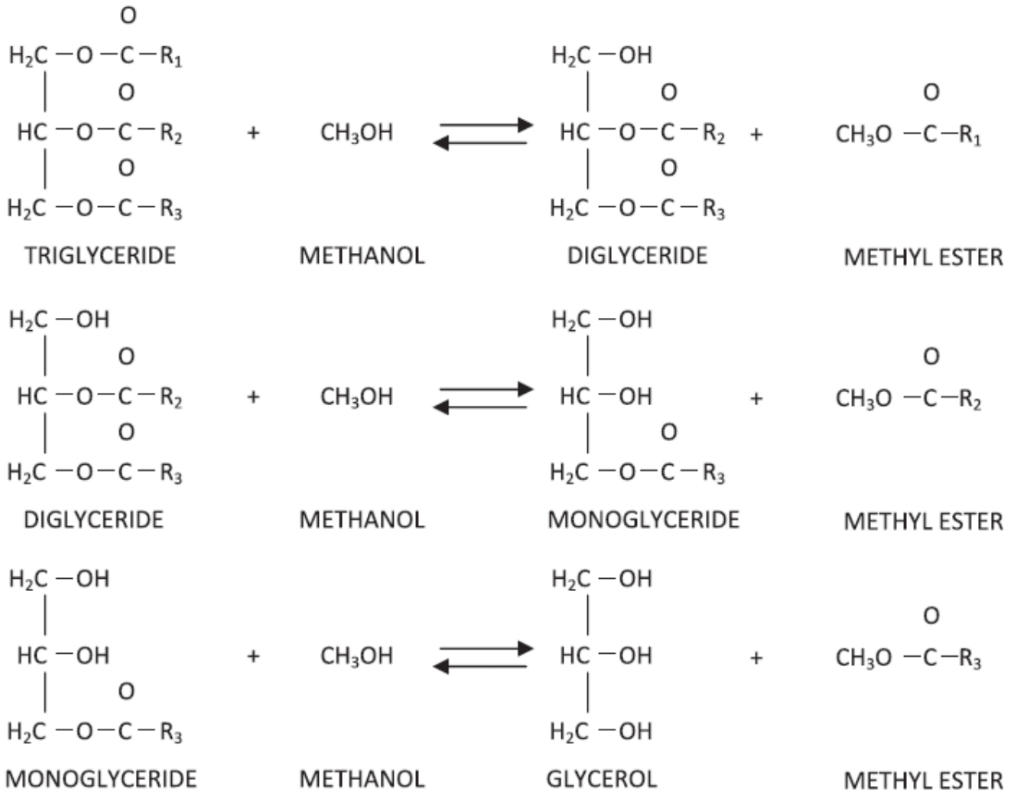


Figure 6: The transesterification reaction [37]

This is because the reactions of the transesterification process are reversible so failing to remove the glycerol and water by-products can have a negative impact on the stability of the fuel. Furthermore glycerol does not add much to the heating value of the fuel but is valuable on its own for other uses and can be commercially exploited.

Water on the other hand can have a range of negative effects on the stability and the quality of the fuel in storage. During storage the water can hydrolyse the methyl and ethyl esters into free fatty acids (FFA). Both the water and the FFA can cause corrosion problems to components of vehicle engines. Furthermore the water tends to separate

from the fuel while in store due to the difference in polarity thus causing problems in the operation of the vehicle.

1st generation biofuels, bioethanol and biodiesel, contain a high amount of oxygen in their structure because of the feedstocks and the processes used for their production. Their feedstocks can have an oxygen content ranging from 10% to 44%, which is only partially removed from the end product, in contrast to petroleum which contains almost no oxygen in the first place [4]. This results in lower energy density (bioethanol 67% less energy dense than gasoline, biodiesel is 90% less energy dense than its fossil counterpart [3]) and induces a range of disadvantages and incompatibilities to conventional fossil fuels, if no measures to improve their properties are taken.

Biodiesel has a number of characteristics in which its properties defer from petroleum diesel the most important of which are summarized in Table 2.

Table 2: Key properties biodiesel [36]

Property	
Oxidation stability	Less stable that fossil diesel especially when there are unsaturated esters
Viscosity	Biodiesel is more viscous than fossil diesel. The viscosity, which depending on the source material can be very high, can lead to solidification of the fuel in low temperatures and cause operational and mechanical problems
Flash point	The flammability of biodiesel is as low as half that of fossil diesel making it safer for storage
Sulphated ash	The inorganic contaminant and soluble metal soap content of the fuel can cause engine deposits and filter clogging
Cetane number	Generally a little greater than diesel
Acid number	The free fatty acids contained in biodiesel can cause corrosion problems
Free glycerol content	Glycerol can cause problems with clogging of the fuel filters of vehicles, due to its polarity and cause coking
Phosphorus content	Can have a negative impact on the exhaust catalyst of vehicles. The content is higher in used cooking oils
Water content	Water in biodiesel can lead to corrosion of engine components, biological growth in fuel storage and to the hydrolysis of the alkyl esters to FFA increasing the fuels acid number

The above make adoption of biodiesel more difficult and spark interest in the possible ways that the biofuel characteristics could be altered to better meet the demands of current technological trends.

Indeed there is a lot of research going on about upgrading the oils extracted from the plants in order to create drop-in biofuels. By drop-in biofuels we mean biofuels, the physical properties of which are so close to their fossil counterparts that it is possible to use them alongside conventional fuel, in mixtures of any proportion, with very little to no modifications required in the existing technology. In essence, R&D has focused on hydroprocessing technologies, where vegetable oils are brought into contact with hydrogen at high pressures and temperatures, that convert the oils into hydrocarbons with the same or very similar composition as those in conventional fossil based fuels. These technologies are described in the detail in the following section.

1.3 Hydrogenation processes for vegetable oil conversion to fuels

In order to produce biofuels of sufficiently high quality, vegetable oils need to be processed so that particular shortcomings can be alleviated. The triglycerides, which make up most of the oil, contain oxygen atoms as Figure 4 shows. Although oxygen contained in a fuel can increase the efficiency of the combustion [38], it is not desirable in fuels for many reasons. Its presence leads to lower energy density as oxygen it-self is the oxidizing agent in combustion and does not contribute to energy storage while it adds weight to the molecules.

The presence of oxygen in the fuel has an effect on the polarity of the molecules. This results in a fuel that is more difficult to mix with conventional fossil fuels, which contain almost no oxygen [14].

The high oxygen content of vegetable oils (up to 50 wt%) has adverse effects, thermal and chemical instabilities, corrosivity, immiscibility with fossil fuels and increase in tendency towards polymerization. [39]

The transesterification process that is the main process used in the industry, currently, for the production of biodiesel leads to a product that has a significant oxygen content. This is because as we saw earlier the process results in a product composed of FAAE which retain two thirds of the original oxygen contained in the triglycerides.

Thus in order to produce drop in biofuels we need to turn to different methods that remove all of the oxygen leaving a product composed of hydrocarbons.

1.3.1 Processes (Hydrodeoxygenation, hydrocracking, hydroisomerization)

In this thesis, the attention is placed on the processes that utilize hydrogen in order to remove the unwanted oxygen, and facilitate the conversion of large hydrocarbons to their isomers or smaller ones that are in the range of diesel but have better characteristics; namely catalytic hydrodeoxygenation, hydrocracking and hydroisomerization.

Hydrodeoxygenation

As was described before, the presence of oxygen in fuels is not a desirable characteristic and removing it is important. Hydrodeoxygenation involves the catalytic reaction between oxygenated molecules with hydrogen in the presence of noble and transition metals such us platinum, palladium and nickel under high pressures and temperatures [40]. During the process hydrogen cleaves carbon-oxygen and carbon-carbon bonds [41]. The result is the removal of the oxygen from the molecules and the production of hydrocarbons, water and carbon dioxide/carbon monoxide.

The reaction between hydrogen and oxygenated molecules can take the path of direct hydrodeoxygenation where hydrogen reacts with the oxygenated molecule to produce water and hydrocarbon with the intermediate formation of alcohol or that of decarbonylation/decarboxylation where the product is carbon monoxide and water or carbon dioxide. The latter path is not desirable as it involves the removal of carbon atoms. An overview of the reactions taking place in the two cases can be seen in Figure 7.

$$\left[CH_3-(CH_2)_m-COOH\right]\xrightarrow{H_2}\left[CH_3-(CH_2)_m-CH_2OH\right]\xrightarrow{H_2}\left[CH_3-(CH_2)_m-CH_3\right]+H_2O$$

$$\left[CH_3-(CH_2)_m-COOH\right]\xrightarrow{H_2}\left[CH_3-(CH_2)_{m-1}-CH_3\right]+CO_2$$

Figure 7: Overview of the reaction pathways of direct hydrodeoxygenation (top) and decarboxylation (bottom)

The metal catalyst also catalyzes reactions that result in the conversion of olefins to paraffins via the hydrogenation of unsaturated bonds. This is a desirable outcome; olefins are detrimental to the quality of fuels since the presence of double and triple bonds be-

tween carbon atoms mean less carbon-hydrogen bonds which are the main energy carriers.

Hydrocracking and Hydroisomerization

Various feedstocks for the production of biofuels as well as other products with important industrial applications like lubricants, give products that suffer in the area of viscosity and other characteristics that are of importance, if they are to be compatible to currently used technology and fuels.

Hydroisomerization is an important process for the upgrade of the characteristics of feedstocks in regard to viscosity, freezing temperature and pour point, especially when the feedstock is rich in long chain n-paraffins. The upgrade is achieved through the conversion of said n-paraffins to their isomers. The resulting mix of mono- or multi-branched paraffins is less viscous and can remain liquid in lower temperatures.

The process of hydrogenation takes place in five stages that are described below:

1. paraffins come in contact with the atoms of a metal catalyst and are dehydrogenated to olefins
2. olefins are absorbed on an acid site where the unsaturated bonds are protonated producing n-alkylcarbenium ions
3. the ions are rearranged to cyclic alkylcarbeniums and
4. undergo β-scission which entails the dehydrogenation and destruction of a C-C bond and the consecutive hydrogenation of the edges of the newly formed branched n-alkylcarbenium
5. the n-alkylcarbenium is then desorbed from the acid site and consecutively hydrogenated into an iso-paraffin by the metal catalyst.

Alternatively the β-scission can take place before the skeletal rearrangement leading to the production of a shorter n-alkylcarbenium and paraffin. In that case instead of hydroisomerization we have hydrocracking which may or may not be desirable depending on the intended use of the product.

1.3.2 Catalysts

The above processes require metal catalysts as well as acid sites in order to take place. Both these requirements are met by the use of bifunctional catalysts. These catalysts are composed of one or more noble metal species, such as platinum loaded on an acidic

support such as Amorphous Silica Alumina (ASA) or various zeolites. The metal sites catalyze the hydrogenation/dehydrogenation reactions, while the acidic sites are required for the skeletal re-arrangement reactions.

The catalysts are required to have large surface area, most of which is provided by the existence of pores. This is important so that there is enough space for the metal atoms to be loaded on the support for the creation of the metal sites that are responsible for the hydro/dehydrogenation.

The ratio of metal to acid sites has been found to have an effect on the quality of the product since it affects the relation between the rates of the hydrogenation and cracking functions which are shown in Figure 8. In general high acid to metal ratio favors hydrocracking while lower acid to metal ratio favors hydroisomerization. In any case, since both metal and acid sites are important for hydroisomerization, a balance between the two functions has to be achieved for optimal results. [42]

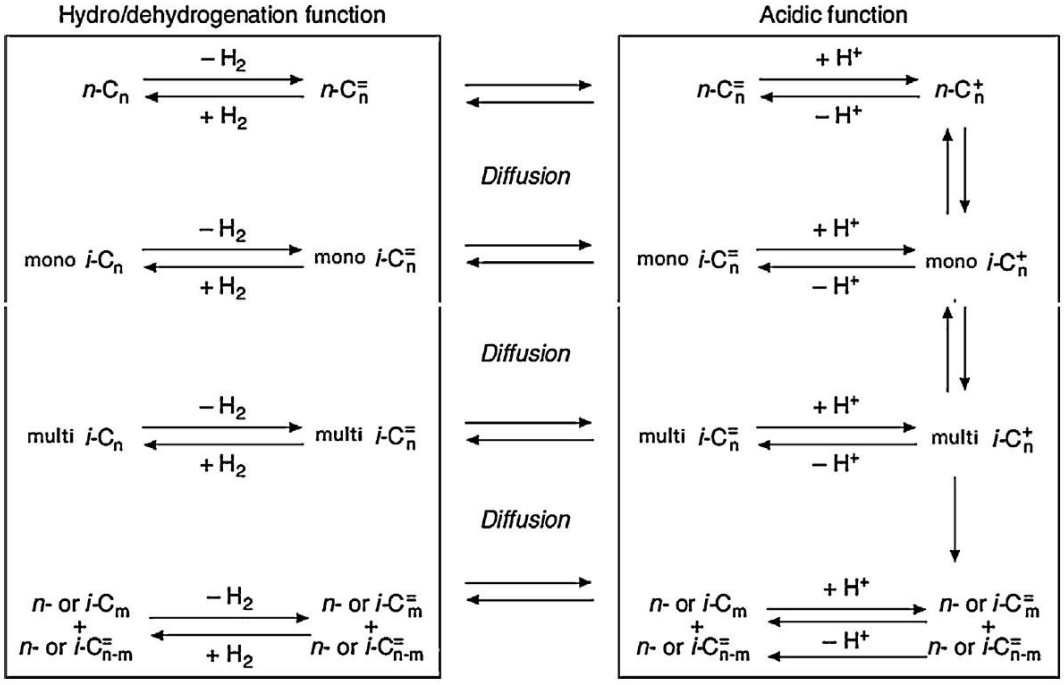


Figure 8: Over view of the bifunctional hydrocracking mechanism reactions [43]

The selectivity of the process towards hydroisomerization of the feedstock as opposed to hydrocracking is influenced by the choice of metal used for hydrogenation/dehydrogenation and the strength/concentration of acid sites on the support. In general noble metals tend to produce better results than non-noble transition metals.

Pore size can also influence the outcome by screening the size of molecules that can enter the pores and interact with acid sites thus protecting branched molecules from further interaction that may lead to cracking. [42]

1.3.3 Commercial status

The processes described above play an important role in the oil refining, lubricant and fuel production industries.

Hydrocracking is used widely in the industry, alone or, in conjunction with hydroisomerization and it can be of great value to profit maximization because it provides a way to turn products of low value and quality into high value ones like diesel and jet-fuel of high quality.

The hydroisomerization process was developed for the purpose of upgrading the quality of lubricants and is used by companies such as Castrol for the production of high quality lubrication products

The processes are important in the utilization of Fischer–Tropsch process. The products of the process are spread in a wide range of carbon numbers and are valuable due to their great quality and the absence of Sulphur, Nitrogen and Oxygen which makes them ideal as drop in fuels that are actually of better quality than the regular fuel with which they are blended. Nevertheless the product is composed of 60 to 80% wax and need to be processed before use to bring their pour point to the desired level [44]. In the process of refining the Fischer–Tropsch process products, Hydrocracking is used to crack the longer carbon chains to produce lighter more valuable products and hydroisomerization is used to improve the cold flow properties of both fuel and lubricant produced, by dewaxing the product.

Incorporating hydrocracking and similarly hydroisomerization, can entail high capital and operational costs, because of the equipment required the cost of the catalyst that can be significant and the cost of the hydrogen feedstock.

Nevertheless advances in technology and the increased availability of natural gas, compared to the past, have made hydrogen more affordable and more readily available. The increasing price of the derived products accompanied by the reduced cost hydrogen and the increasing interest in making use of lower quality and difficult to process feedstocks like vacuum gas oil, oil sand and oil shale, make the application of the hydrocracking process increasingly more appealing and viable economically.

Indeed hydrocracking has been enjoying increasing attention and utilization and has even replaced Fluid Catalytic Cracking (FCC) in some newer installations.

The catalyst can represent a significant fraction of the cost of incorporating hydroprocessing in a refinery. Catalyst optimization is very important as it can have a great impact in the yield and value of the resulting products. Due to the peculiarities of the different feedstock mixtures that are used as well as the intended properties of the products, the same type of catalyst used cannot be used in every different instance. Instead, different tailor made catalysts are used in each process and installation so that value is maximized for the particular feedstocks and intended products. Developing a catalyst that can maximize yield and quality is a cost intensive process but the efficiency gains outweigh the development and production costs.

1.4 Castor beans as a feedstock for 2nd generation biofuels

Castor beans come from the plant *Ricinus communis*. It is commonly known as castor plant and its cultivation by humans goes back to the ancient times [45]. It is found growing in tropical and subtropical regions as it requires warm climates and cannot germinate when ground temperature drops below 16 °C.

Plants of the species can grow as tall as 10m [46] although cultivated varieties are usually between 0.6 to 2.5m. Their cultivation is mainly exercised in countries like India (which is the larger exporter of castor oil), China, Brazil and Mozambique. Harvest of the beans is done either manually from semi-wild plants (which as we will see is a potentially dangerous occupation) or by mechanical means, from plants varieties that lend themselves to mechanized cropping. The yield achieved can be affected by many factors. In order to achieve maximum yield the plants need to grow at 20-26°C and at low humidity [47]. The yield may be adversely affected by the length of daytime, possible infestations by insects, more than a hundred species of which can feed on the plant, diseases, lack of water, extremely elevated temperatures and increased water salinity [45].

The plant is not as widely cultivated nowadays as it could be because of its toxicity to humans and animals [48] [49]. The ricin (a toxic glycoprotein) contained in castor beans is extremely poisonous [50] and is claimed to have double the toxicity of cobra venom [45]. Nevertheless, the oil extracted from the beans of the plant has been used for mil-

lennia as medicine [51], cathartic, lamp oil [45], cosmetic products ingredient [52], lubricant and in various other industrial products [47] and even labour inducing drug [53].

Today the main motive for the cultivation of castor plants is the high oil content of the castor beans that can be as high as 58% and its use as a lubricant. The oil, mainly composed of the triglycerides shown in Figure 9, is also used in a variety of applications from medicine to industrial chemicals. Thus significant plantations exist mostly in India.

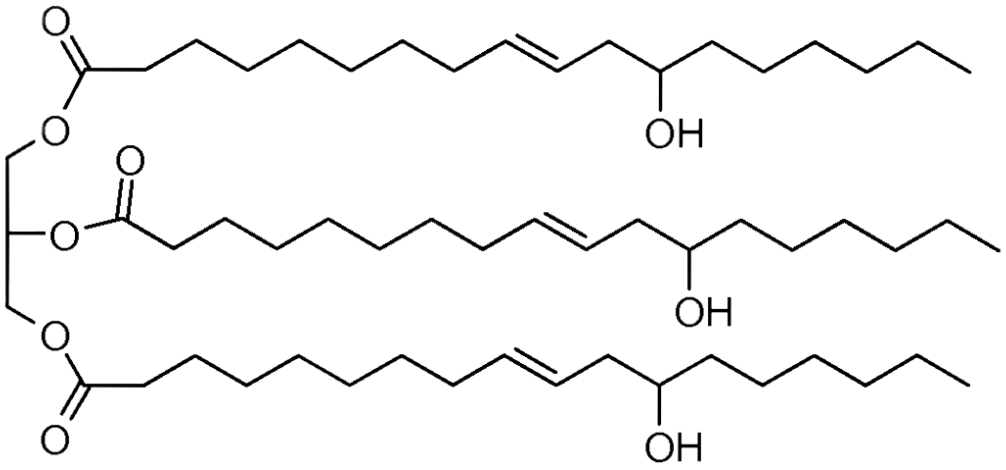


Figure 9: Triglyceride of castor oil

The extraction of the oils is done, initially, through the use of mechanical pressure. The beans are crushed and dried before being pressed to extract the oils. This process is preferred when the product is to be used for pharmaceutical purposes [46] however it is not sufficient to extract all the oil; in fact most of it remains in the cake of pressed beans. In order to claim the remaining oil, solvents like heptane are used to wash the oils out of the cake [47]. By the end of the process 98-99% of the available oils are claimed. The oils are then refined to resist degradation in long term storage although this is not necessary if they are stored under airtight conditions [46].

The residues of this process are highly toxic and cannot be used, as they are, for agricultural purposes. Nevertheless they can still be of value as there are ways to detoxify them and use them as fertilizer or animal feed and there are reports of successful use of untreated, toxic, castor bean waste for the production of useful products like enzymes [54]. Unfortunately detoxification of the toxic cake that results from extraction of the oils is not always carried out properly and the resulting products have some degree of toxicity, leading to cases of animal poisoning [55].

The resulting product is a yellow-green odorless oil mixture very rich in ricinoleic acid (in triglyceride form shown in **Error! Reference source not found.**)which represents 84-90% of the fatty acid content; although there is a variety of the beans that gives an oil product which is mainly (78%) composed of oleic instead of ricinoleic acid [45]. Properties, of castor oil, which pertain to its use as a fuel or as a feedstock for biofuel production can be found in Table 3.

Table 3: Properties of castor oil [46]

Property	Value	Unit
Density (15 °C)	950-974	Kg/m^3
Flash point according to P.-M.	229-260	°C
Kinematic viscosity (40 °C)	240-300	mm^2/s
Net calorific value	37.2-39.5	MJ/Kg
Flammability (cetane number)	42	-
Coke residues	0.22	%
Iodine number	82-90	g/100g
Sulphur content	10	mg/Kg
Total impurities	ca. 10	mg/Kg
Neutralization value	1-4	mgKOH/g
Oxidation resistance (110 °C)	95	H
Phosphorous content	<4	mg/Kg
Total content of Mg und Ca	-	mg/Kg
Ash content	<0.01	%
Water content	0.15-0.3	%

An important property of the oil, as far as its use as fuel and biofuel feedstock is concerned is it kinematic viscosity. The oil is unusually viscous; so much so that it is well outside of the desired range for diesel [47]. The high viscosity is thought to be the result of the presence a hydroxyl group on the 12^{th} carbon atom of the fatty acids [46]. Actually, castor beans are the most important source of hydroxylated fatty acids [56].

The interest in converting castor oil to fuels stems from the following: (1) castor bean is a crop with high yields and low irrigation needs; (2) castor beans have high oil yields; (3) it is non-edible and thus does not compete with the food chain and (4) the main fatty acid contained in castor oil, ricinoleic acid with a molecular formula $C_{18}H_{34}O_3$, has a

hydrocarbon chain which falls in the diesel category and thus with proper processing with the technologies presented in paragraph 1.3 can result in high diesel production.

1.5 Summary & Scope of the dissertation

Renewable sources of energy are believed by many to be the future of energy production, holding the promise of clean abundant energy economic growth, energy security and sustainability.

In this framework, the interest in biofuels keeps rising and is expected to continue doing so, pushed by regulators around the world. In the European Union, directives on renewable energy obligate member states to fulfill quotas on renewable energy penetration ensuring continuous efforts for the development and commercialization of biofuels.

Currently, in Europe, most of the attention is placed on biofuels produced from 2nd generation biomass sources that have minimal impact of the food supply chain and are much more energy dense than 1st generation ones.

According to the European Environmental Agency's (EEA) National Renewable Energy Action Plan (NREAP), it is expected that by 2020, 90% of the total renewable energy consumption in the transport sector will come from biofuels, in particular from biodiesel [10]

For practical and economic reasons it is desirable to be able to co-process biomass for the production of biofuels along with regular petroleum, to minimize cost by making use of the vast existing infrastructure for fuel production and distribution. Furthermore the ability to use biofuels in conjunction with regular fossil fuels with minimum or no complications and modifications on existing technology is very important for their establishment in the market. For these reasons, R&D funding has been directed towards developing a variety of technologies and processes for the refinement of the characteristics of biofuels and their integration to fossil fuel production.

Castor oil lends itself to this purpose by being a relatively easy to handle, 2nd generation source of fatty acids in the range of diesel that can be available in significant quantities and can be incorporated to existing fuel production infrastructure. Interest in its utilization as a feedstock for fuel production has led to intensified research interest in both the academic and commercial realms.

The research conducted in this thesis falls within the scope of investigating the feasibility of co-processing castor oil together with fossil-based refinery feedstock in conven-

tional hydroprocessing units for the production of high quality diesel fuels. The hydrogenation of vegetable oils to diesel fuel has been demonstrated in the past. A main issue with the produced fuel is its bad cold flow properties due to the high percentage of linear paraffins in the fuel (that originate from the fatty acids' hydrocarbons chains). In order to overcome this issue, it is necessary to isomerize part of the linear paraffins to isoparaffins, which demonstrate improved cold flow properties. Commercial isomerization catalysts are optimized for C_5/C_6 alkanes. The major difficulty in the hydroisomerization of n-alkanes with more than six carbon atoms is their pronounced tendency to cleave. Therefore new catalysts, suitable for isomerization of diesel-range paraffins should be developed. The main purpose of the thesis is to synthesize, characterize and test novel catalysts with high activity and selectivity for the isomerization of castor oil and castor oil-derivatives. The results can be used to further understand the impact of utilizing castor oil in existing catalytic hydrotreatment processes and improving/developing new catalysts for such processes.

2 Experimental part

The experimental work was conducted in the Laboratory of Environmental Fuels and Hydrocarbons (LEFH) in CPERI/CERTH. The following sections describe the experimental procedures for the synthesis, characterization and testing of the catalytic materials investigated in this work for the hydrocracking/isomerization of castor oil to hydrocarbon fuels.

2.1 Catalyst synthesis

Catalyst synthesis included the preparation of the following mono- and bimetallic Pt-based catalysts supported on amorphous silica-alumina (ASA): 0.1 wt% Pt/ASA, 0.1 wt% Pt-0.1 wt% Ir/ASA and 0.1 wt% Pt-0.1 wt% Pd/ASA. The catalysts were synthesized via dry impregnation of the noble metal on the support. The precursor compounds employed were $H_2PtCl_6 \cdot 6H_2O$ (Merck KGaA, ~40% Pt), $Pd(NO_3)_2 \cdot xH_2O$ (Alfa Aesar, 99.9%,~39% Pd) and $IrCl_3 \cdot H_2O$ (Merck KGaA) for Pt, Pd and Ir, respectively. For the monometallic catalyst, the appropriate amount of the Pt precursor compound was diluted in a specific amount of doubly distilled water, equal to the amount of pores of the support. The solution was then added drop wise to the support, with careful mixing in order to achieve homogeneity. In the case of the bimetallic catalysts, the noble metals were added to the support sequentially, first Pd or Ir and then Pt, with an intermediate drying step. In all cases, the resulting paste was dried at 120°C for 2 hours and was then calcined at 400°C for 3 hours in synthetic air.

In addition to the three aforementioned catalyst two extra catalysts containing iridium and platinum were synthesized to test the effect of impregnation order. The original catalyst was synthesized by first impregnating the support with Ir and then with Pt. In the case of the two additional catalysts the order was changed. One of the catalysts was synthesized by impregnating first with Pt and then with Ir, while the other was impregnated simultaneously with both metals (this is denoted by the parenthesis in the name of the catalyst).

2.2 Catalyst characterization methods

Before being used as well as after the experiments, were conducted, the various catalysts were studied using a variety of analytical methods [57] to determine their quality. The catalysts underwent the following analysis:

Fresh samples:

- BET analysis to determine the surface area per gram of catalyst, available for the catalytic reactions: Surface areas of the samples were determined by N_2 adsorption at 77 K, using the multipoint BET analysis method, with an Autosorb-1 Quanta chrome flow apparatus. Prior to the measurements, the samples were dehydrated in vacuum at 250°C overnight. The Brunauer–Emmet–Teller (BET) equation was used to calculate the apparent surface area (S_{BET})
- Porosity analysis to determine the volume, available to the reactants to enter the catalytic particles, per gram due to the porous structure of the catalyst: The pore volume was measured by N_2 adsorption/desorption using the method described above for the surface area. The micropore volume (V_{micro}) was calculated via the t-plot method.
- Inductively coupled plasma to determine the actual metal loading on the impregnated catalyst: Inductive coupled plasma-atomic emission spectroscopy (ICP-AES) was performed on a Plasma 400 (PerkinElmer) spectrometer, equipped with Cetac6000AT+ ultrasonic nebulizer.
- FTIR Pyridine Adsorption analysis to determine the concentration and type of acid sites on the catalytic surface: IR spectra were collected using a Nicolet 5700 FTIR spectrometer (resolution 4 cm−1) by means of OMNIC software. Data processing was carried out via the GRAMS software. The samples were finely ground in a mortar and pressed in self-supporting wafers (~15 mg/cm2). The wafers were placed in a homemade stainless steel, vacuum cell, with CaF2windows. High vacuum was reached by the means of a turbo molecular pump and a diaphragm pump placed in line. The infrared cell was equipped with a sample holder surrounded by a heating wire for the heating steps and connected to the vacuum line, which was also heated in order to avoid pyridine condensation or its adsorption on the walls. Before IR analysis, all samples were heated at 450°C under high vacuum (10−6mbar) for 1 h in order to desorb

any possible physisorbed species (activation step). All spectra were collected at 150◦C in order to eliminate the possibility of pyridine condensation. Initially, the reference spectrum of the so-called activated sample is collected. Then adsorption of pyridine is realized at 1 mbar by equilibrating the catalyst wafer with the probe vapor, added in pulses for 1 h. The desorption procedure of pyridine is step wisely monitored by evacuating the sample for 30 min at 150, 250, 350 and 450◦C and cooling down to150◦C after each step to record the corresponding spectrum

Used samples:

- CHN elemental analysis to determine the amount of carbon and hydrogen that deposited as coke on the catalyst during the experiments: Analysis was performed with a LECO-800 CHN analyzer on all catalytic samples after the hydroisomerization reaction.
- Temperature Programmed Oxidation (TPO) to acquire information on the qualitative characteristics of the coke formed on the used catalyst: Temperature programmed oxidation (TPO) was performed on an STA 449 F5 Jupiter, thermogravimetric analyzer to obtain information on the amount and nature of coke deposited on the catalytic surface during reaction. The method works by recording the weight of the catalyst during exposure of the coked catalyst in a chamber under controlled atmosphere and temperature conditions. The atmosphere inside the chamber can be pure oxygen or mixture of oxygen and nitrogen (air) and the temperature is set to progressively rise at some defined rate until some upper limit. The outcome is the weight loss of the sample with temperature, which is indicative of the removal of the carbon and its conversion to CO_2 via its reaction with oxygen. Typically, 20–30 mg of the sample was loaded into an alumina crucible, and the temperature was raised from room temperature to 900°C at a heating rate of 10°C/min in synthetic air flow. The system was maintained isothermally at 900°C for 30 min.

2.3 Catalyst testing

The catalysts investigated in this thesis were tested under the same conditions in order to determine their appropriateness for use in the hydroisomerization of diesel range feedstocks. For this reason a variety of feedstocks were used. All the catalysts under-

went testing, using n-Hexadecane as feedstock in order to determine the one with the greatest potential. Then the catalyst that was deemed most appropriate was tested with n-Heptadecane and later with a feedstock more indicative of those that would be encountered in a refinery.

2.3.1 Feedstocks

During the experiments conducted for this thesis, four different feedstocks were used; three liquids and one gas. The gaseous feedstock was pure hydrogen. The three liquid feedstocks were n-Hexadecane, n-Heptadecane and a diesel fuel produced from the hydrocracking of a mixture of 5 wt% Castor-oil and 95 wt% VGO.

Hydrogen

The presence of hydrogen was needed both in the process of the activation of the catalysts and in the hydrocracking/isomerization of the liquid feedstocks since the reactions take place in a high pressure, pure hydrogen, atmosphere.

N-Hexadecane

N-hexadecane was used as model compound for castor oil for catalyst screening purposes. In order to screen catalysts, a large amount of liquid feedstock of well-known characteristics is required. N-hexadecane is an appropriate model compound since it is representative of the chain length in castor oil fatty acids, while being light enough to be in liquid phase in the ambient temperature of the lab (melting point = 18 °C) and in gas phase in the temperature of the reactor (boiling point = 287 °C). Moreover, it generates a product distribution that is simple enough to be quantified rapidly using analytical GC.

N-Heptadecane

N-Heptadecane was used as feedstock with the optimum catalyst in order to gain information on the effect of the length of the hydrocarbon chain on the hydroisomerization process.

Diesel from hydrocracked 5 wt% castor oil – 95 wt% VGO

The optimum catalyst identified from the experiments with n-hexadecane was also tested using a more realistic feed, consisting of the diesel product derived from the hydrocracking of 5 wt% castor oil – 95 wt% Vacuum Gas Oil (VGO). This diesel fraction is representative of the hydrocarbons that need to be isomerized to improve the cold flow properties of castor oil-derived biofuels. Hydrocracking was performed in pilot

scale high pressure unit in CPERI/CERTH using conventional refinery catalysts and feed.

2.3.2 Description of the reactor unit

The isomerization experiments were conducted on a small scale high pressure fixed bed reactor unit. A picture as well as a simplified schematic of the unit, showing the most important parts of the setup, is shown in Figure 10.

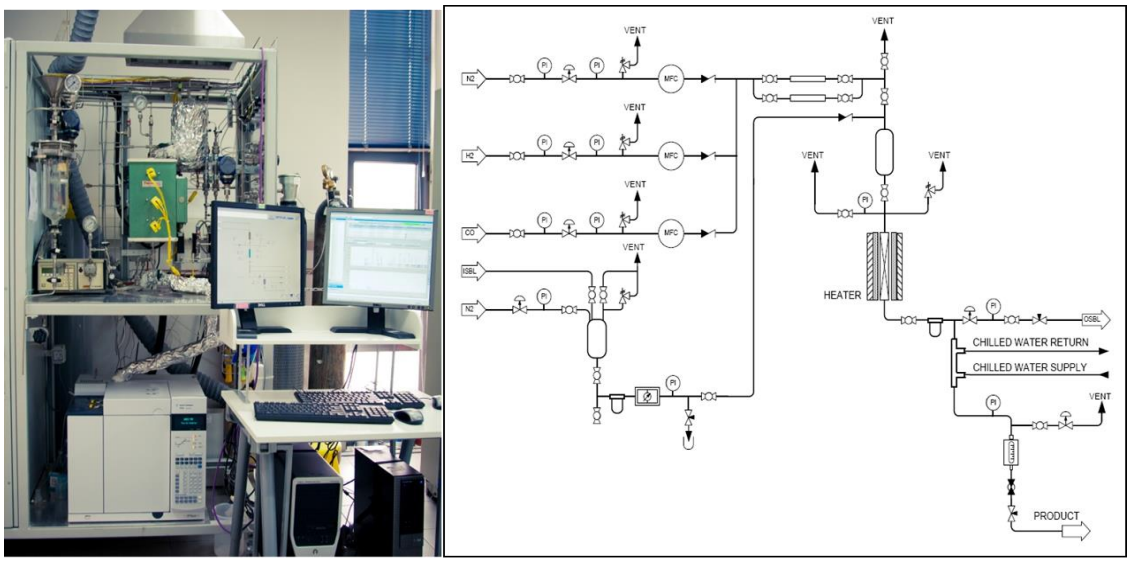


Figure 10: Picture and schematic representation of the unit used for the experiments (the CO inlet was not active in the experiments of this thesis)

The unit is equipped with four inlet streams, one for the liquid feedstock and three for gaseous feedstocks. The liquid feedstock is contained in a 3 lt glass vessel and its flow is controlled via a high precision Gilson-type pump. The gaseous flows (hydrogen as reactant and nitrogen as purge) are regulated through electronic mass flow controllers. The liquid and the gas flows are mixed in a pre-mixing vessel and the mixture is then introduced to the reactor. The reactor is a fixed bed stainless steel reactor, with 9.3 mm ID and 48cm length, heated by a three-zone furnace that allows good control of the operating temperature. The temperature of the reactor is measured by a thermocouple, contained in a thermowell located in the middle of the catalytic bed. The catalyst packing is shown in Figure 11. The catalyst sample (3g) was diluted with an equal amount of SiC to achieve isothermal operation. The catalyst/SiC mixture was placed in the middle of the reactor, with SiC added before and after the bed as packing material.

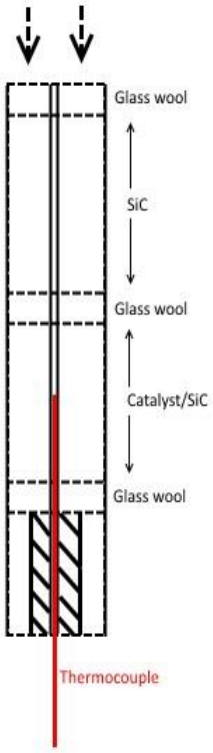


Figure 11: Schematic representation of the reactor setup

After the reactor, the unit has a product separation section. The reaction products are first cooled via a heat exchanger and are then directed to a gas-liquid separator. Steady-state activity measurements are taken after at least 8 h on stream, collecting and analyzing both liquid and gaseous product samples. The liquid samples are analyzed with PIANO analysis, while the composition of the reaction off-gases is detected by gas chromatography. The test facility can operate to a temperature range up to 600°C and pressures up to 100 atm.

2.3.3 Experimental procedure and conditions

Before each experiment, approximately 3 g of catalyst, previously dried overnight and diluted with equal amount of SiC, was loaded into the reactor. The catalyst was activated in situ in hydrogen flow at 400°C for 2h, by raising the temperature with a heating rate of 5°C/min. Thereafter the system was pressurized in hydrogen and stabilized at the desired reaction temperature and pressure. The tests were performed under standard op-

erating conditions at pressure 20bar, temperature 310°C and WHSV 2-8 h^{-1}. In all experiments the H_2/HC molar ratio was kept constant and equal to 7.5. Steady-state activity measurements were taken after at least 8 h on-stream, collecting and analysing both a liquid and a gaseous product sample. The liquid samples were analysed with PIANO analysis (hydrocarbon analysis carried out by GC to determine the amount of paraffin (P), isoparaffins (I), aromatics (A), naphthalene (N), and olefins (O)), while the composition of the reaction off-gases was detected with a GC.

After the end of the test, the catalyst/silicon carbide mixture was carefully retrieved and sieved using an appropriate sieve in order to separate the catalyst from the silicon carbide. The catalyst was kept for further testing, in order to determine the amount of coke deposited on the surface.

3 Catalyst characterization

In the following section, a brief description as well as the results of the catalyst characterization analyses are presented.

3.1 Surface area & Porosity

The surface area is an important property in catalysis, as it is a measure of the concentration of exposed active sites. In the case of the bifunctional catalysts of this thesis, this corresponds to (de)hydrogenation sites (noble metal) and acid sites. Likewise, the porosity of the catalytic materials is a very important characteristic that can have negative or positive impact on the catalytic activity depending on the conditions of the reactor environment and the feedstocks used. The presence of pores greatly enhances the surface area available to carry metal and acid sites while helping to keep the volume and weight of the material as low as possible. This happens because pores of the catalytic particles allow the reactants to enter the particle and the walls of the pores serve as carriers of metal and acid sites.

The size and structure of the pores [58] play an important role in the reaction rates that can be achieved through the limits they impose on the diffusion of the reactants inside the particle. In order to maximize the rate of the reactions, the size of the pores needs to be large enough so as not to hinder diffusion of the reactants and products through the particle. The pore size required depends on the size and characteristics of the molecules involved, while the pores also need to have a high degree of interconnectivity. Ultimately the optimum porosity is a balance between having enough space for diffusion to work but not so much as to waste volume and compromise the mechanical strength of the particle.

Figure 12 shows the surface area and porosity analysis results of the particles of the catalysts as well as the support alone for comparison.

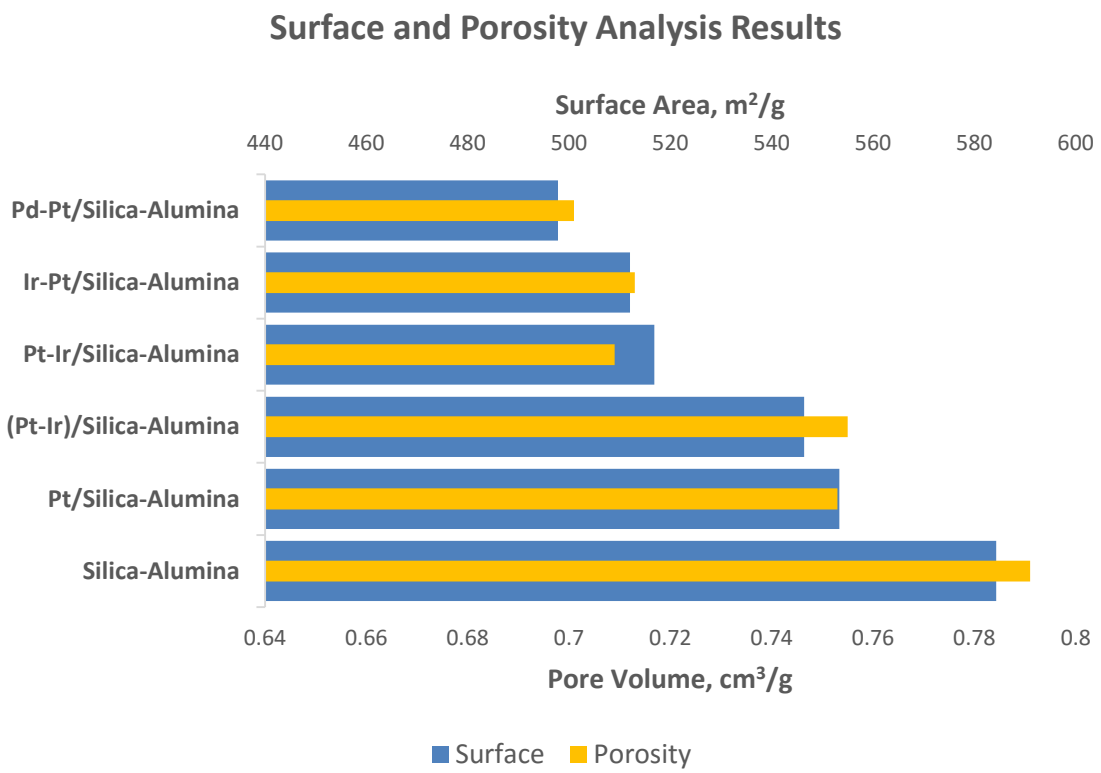


Figure 12: Comparison of the surface area and pore volume of the catalysts and the support

The results of the BET analysis show differences between the surface areas of the analysed materials. The difference in surface area ranges from 5% to 15% compared to the support. Additionally the catalysts seem to be grouped in couples. Pt is relatively close to (Pt-Ir), followed by similar values for Pt-Ir and Ir-Pt, with finally Pd-Pt having the smallest surface area. The decrease of the surface area in the mono- and bimetallic catalysts compared to the pure support can be attributed to the calcination of the materials at 400°C, a process which causes some sintering and agglomeration. Additionally, the deposition of the active metal on the support can plug some of support's pores, leading to the decreased surface area. [59] The differences in the surface area can also be related to the amount of metal on the catalyst, since the surface area is generally lower for the bi-metallic catalysts that have double amount of metal compared to the monometallic Pt/ASA catalyst.

Concerning the porosity results, the silica-alumina support in its pure form appears to have the highest porosity while the catalysts lack significantly. A comparison between the porosity results and the surface area of the catalysts makes the connection between porosity and available surface obvious. The materials with the higher degree of porosity are also the ones with the highest available surface area. The decrease of porosity in the

catalysts compared to the support can be again related with the heat treatment that the catalysts have undergone.

The original support was measured as received, while in the case of the catalysts the materials underwent one and/or two calcination steps de-pending on the number of impregnated metals. The process of calcination exposes the solid powder to high temperatures that can cause sintering resulting in lower porosity. This explains the observed order of porosity, with the pure support being the most porous followed by the monometallic platinum catalyst (one calcination step) and then the bimetallic catalysts (two calcination steps). Nevertheless the bimetallic catalysts exhibit differences in porosity among them, with the order of Ir deposition on the sur-face affecting the final surface area and porosity of the catalyst. A possible explanation may be that the process of the metal addition leads to clogging of part of the pores. The resulting porosity reduction would be the combined effect of the metal loading and the sintering effect of the heat treatment.

3.2 ICP

ICP was employed to determine whether the intended noble metal loading was achieved in the final materials. Figure 13 shows the results of the ICP analysis on the amount of platinum and palladium loaded to the different catalysts. Results on iridium are not presented, due to technical limitations of the method in the measurement of iridium.

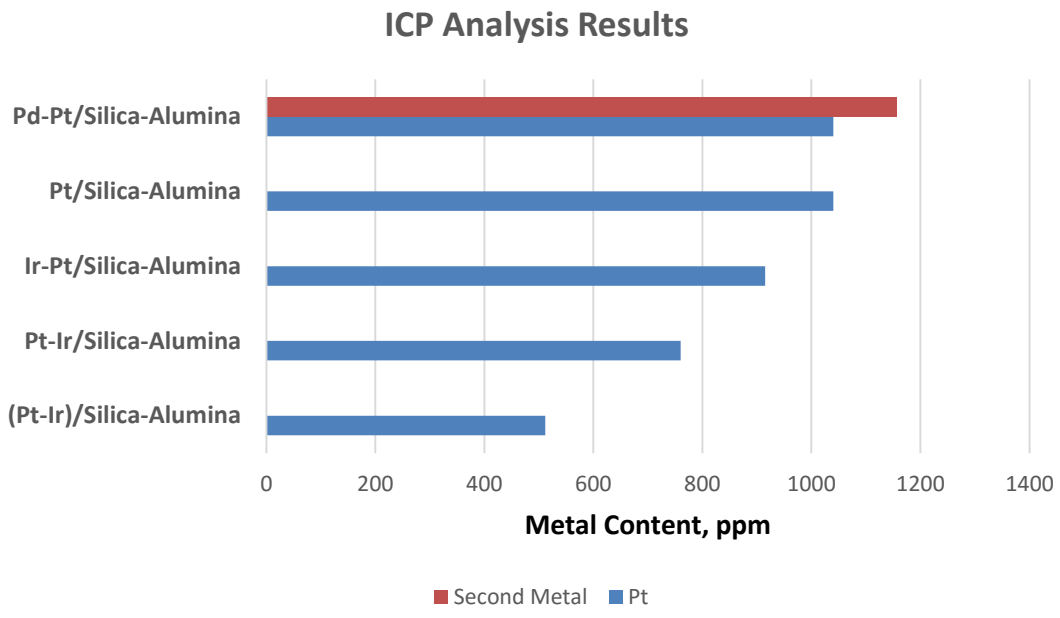


Figure 13: Comparison of the metal content of the different catalysts and the support used

Platinum wise, the Pt and Pd-Pt catalysts appear to have the same metal uptake while the three Ir/Pt variants appear to have an uptake as low as half, that of the other catalysts.

The type of secondary metal seems to have an effect on the amount of Pt that is eventually loaded on the catalyst. Specifically adding Pd does not seem to adversely affect the uptake of Pt. On the other hand Ir seems to negatively affect Pt uptake as all three Ir variants have lower Pt content.

The impregnation sequence also appears to have an effect on Pt uptake. The catalyst that underwent simultaneous impregnation appears to have retained much less (almost half) of the available Pt. On the other hand, sequential impregnation gave better results Impregnating first with Ir and then with Pt had a smaller effect on the result than going with Pt first.

This apparent difference in the uptakes can be attributed to the interaction between Pt and Ir molecules that can lead to the creation of insoluble alloys, so that even though the uptake is, largely, probably the same, the results give the impression of a lower platinum uptake.

This does not seem to affect all the Ir/Pt catalyst in the same extend. The catalyst that was made via simultaneous impregnation is the one that is most affected while in the other two cases more Pt shows up in the analysis although there is difference between them as well, so it seems that impregnation order matters.

On the surface of the support, platinum and iridium have been found to interact and form bimetallic clusters [60] [61] along with monometallic sites. The calcination step has been observed to induce the formation of large iridium crystallites (IrO_2). In general the surface of the catalyst is characterized by the existence of, very, dispersed platinum sites, large iridium crystallites and bimetallic clusters where platinum is dominant. [62]

Bearing the above in mind the discrepancy between the three catalysts can be explained in the following manner. On the simultaneously impregnated catalyst, during impregnation, both metals are dispersed in a soluble form in the impregnating liquid and thus are given the chance to interact with each other more freely. Thus greater amounts of the alloy can be created.

In the case of the sequentially impregnated catalysts, by the time the second metal is added the first has already been dispersed on the surface and formed metal sites. In the case where Pt is added first the metal is highly dispersed and covers a large area on the

surface. When iridium is added it able to interact with the dispersed Pt albeit in to a smaller extend as the Pt atoms are already in place and less available for interaction. In the case where iridium is added first, it tends to form a smaller number of bigger crystallites and thus when platinum is added it is dispersed and able to avoid the less dispersed iridium to a greater extend.

In the case of the Pd-Pt, solubility is not a problem and the interaction between the two metals leads to a different distribution of atoms on the surface. The surface of such catalysts is characterized [63] by the existence of monometallic Pd sites that coexist with bimetallic Pt–Pd clusters. The bimetallic clusters are composed of a core rich in platinum covered by surface that is rich in palladium. The Pt atoms are exposed to the surface to different degrees depending on the composition of the acidic support. [63]

Additionally comparing the surface area and metal uptake results, for the three Ir/Pt catalysts, we see that lower surface area is accompanied by lower apparent platinum uptake this observation is in agreement with the above, as the lower surface area means less space for the metal atoms to disperse and so may promote the creation of Ir/Pt alloy.

It is worth noting that there is a quantitative discrepancy between the metal loads of the, different, catalysts even without taking the metal uptake into account. This is because even though the amounts, used, were calculated to impregnate the support with 0.1%wt of each metal, the amount of atoms available for uptake was different between the cases of pure Pt, Pd-Pt and the three Ir variants.

This is because the Pt catalyst was only impregnated with one metal so almost half of the amount of metal was available compared to the three Ir/Pt catalysts. Additionally, due to Palladium having a significantly lower atomic weight than Platinum and Iridium the 0.1%wt means that almost 170% more metal atoms were available during impregnation of the support for the Pd-Pt catalyst, compared to the case of the pure Pt catalyst and almost 35% more, compared to the Ir/Pt catalysts.

3.3 Acidity

As was described before the acidity of the bifunctional catalyst and its balance with the activity of the metal sites is very important to the performance of the catalyst and can have a significant impact on selectivity and conversion. The total acidity, type and acid

strength distribution of the acidic support were measured by the FTIR-pyridine adsorption technique. The resulting data are shown in Figure 14.

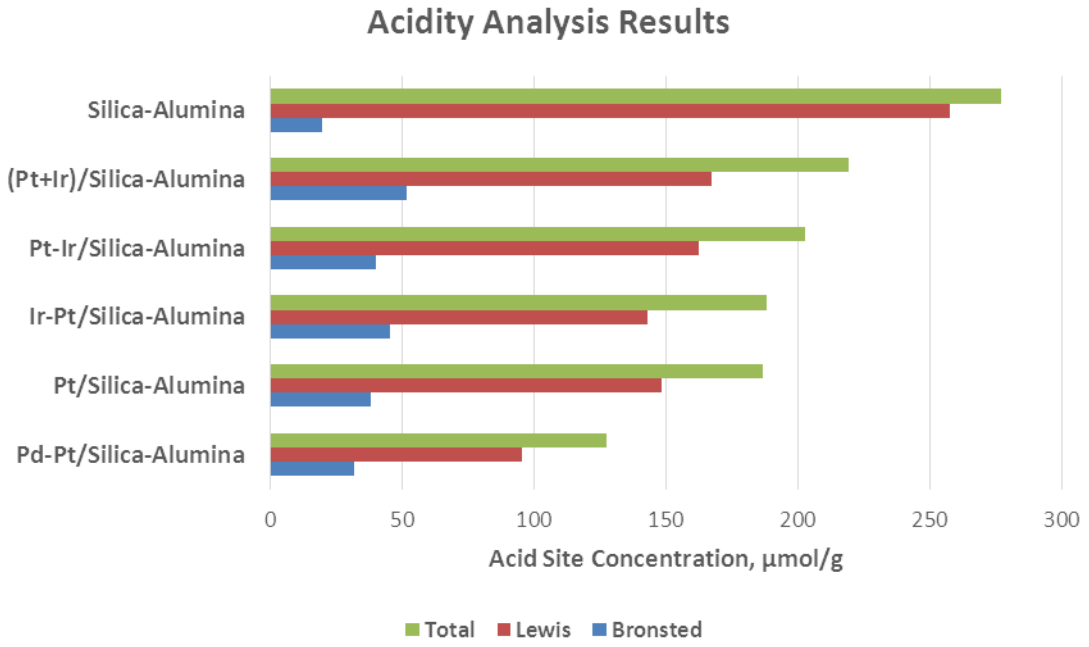


Figure 14: Comparison of the acidity of the different catalysts and the support used

Silica-Alumina that has the highest surface area is the most acidic one since the larger surface allows for more acid sites.

Additionally this acidity is provided mostly by Lewis acid sites, with Brønsted sites amounting to only about 7% of the total. A summary of the percentage of Brønsted and Lewis acidity is presented in Table 4.

Table 4: Brønsted and Lewis acidity percentages for the different catalysts

Catalyst	Lewis Acidity, %	Brønsted Acidity, %
Pd-Pt/Silica-Alumina	75	25
Ir-Pt/Silica-Alumina	76	24
(Pt-Ir)/Silica-Alumina	76	24
Pt-Ir/Silica-Alumina	80	20
Pt/Silica-Alumina	80	20
Silica-Alumina	93	7

As surface area decreases acidity follows with the notable exception of the Pt catalyst that has the highest surface area among the bifunctional catalysts but the second lowest acidity as shown in Figure 15

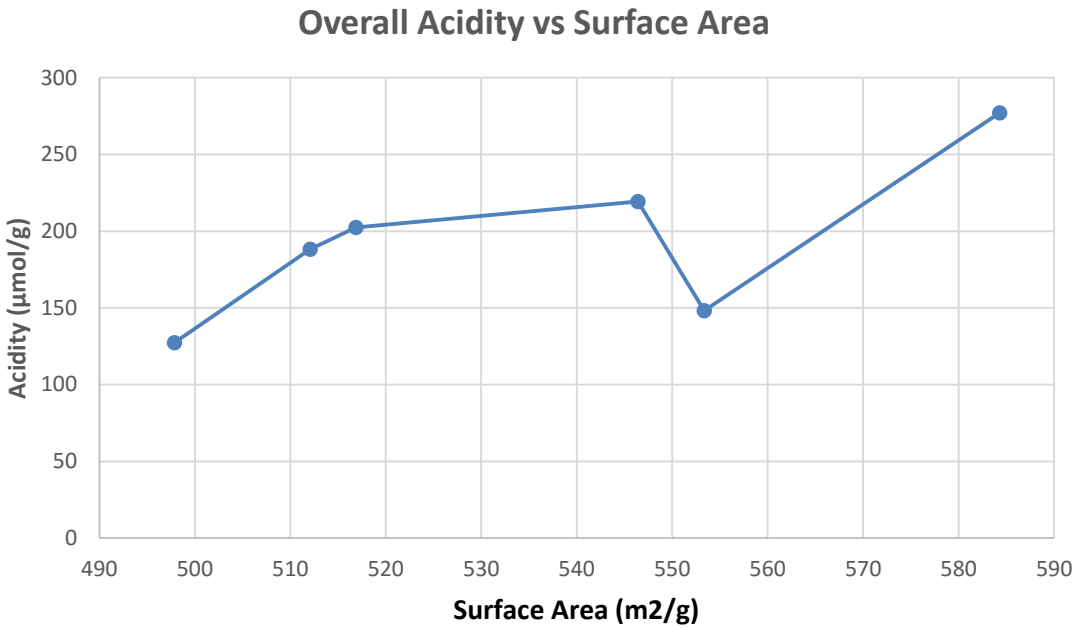


Figure 15: Overall acidity vs surface area comparison between the different catalysts

Furthermore, the impregnation of the silica-alumina support with platinum appears to increase both the total number and percentage of Brønsted acid sites. The inclusion of the second metal further increases Brønsted acidity, both in the case of Ir and Pd while Lewis acidity is decreased along with overall acidity.

These results are in agreement with the results of other studies in which the sequential as well as the simultaneous impregnation of a WZ catalyst with Pt and Pd have led to a decrease of the overall acidity of the catalytic material and an relative increase of mild acid sites. [64] [65]

Additionally loading acid supports with Pt alone has also been observed to reduce overall and Lewis acidity and increase Brønsted acidity. The effect has been attributed to the metal being able to neutralize Lewis acid sites (although it can function as electron acceptors) and to modification of the acid support during impregnation that leads in the creation of more Brønsted acid sites. [59] This could explain the significantly reduced acidity of the Pt catalyst that is not in agreement with its high surface area.

The distribution of the Lewis and Brønsted acid sites in terms of strength is an important characteristic pertaining to the activity and selectivity of the catalyst. As Figure

16 and Figure 17 show, their distribution, in the cases examined, in relation to strength is very different.

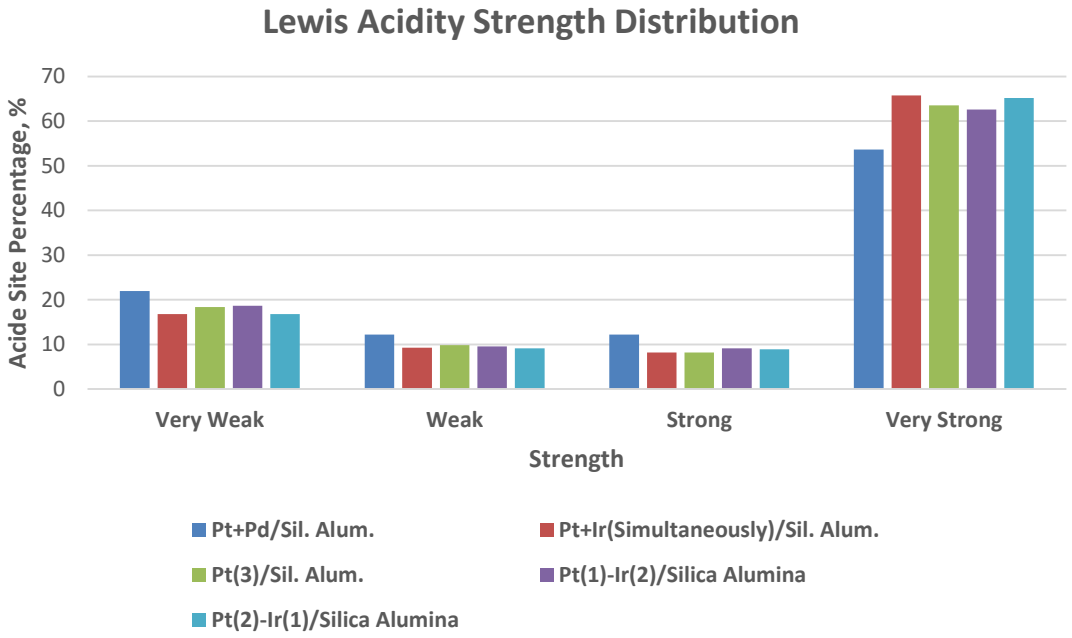


Figure 16: Distribution of the strength of Lewis acid sites

Lewis acid sites are predominantly very strong, with more than 50% belonging in that category while the rest are more or less equally distributed in the other three levels of strength. This can have a negative effect on the rate of the reactions because it is harder for the molecules to desorb from strong acids sites. [66] Thus the presence of a lot of strong and very strong acid sites has been shown to lead in lower selectivity to isomerization, as the increased residence time of the molecules on the acid sites due to the strong adsorption favors further cracking reactions to smaller molecules. Additionally this characteristic favors the formation of coke that serves to progressively deactivate the catalyst. [65]

On the other hand Brønsted acid sites are predominantly weak but distributed in a linear ascending manner from very strong to very weak. This is good as mild Brønsted acidity strength is favorable to selectivity. [65] Nevertheless in both cases all catalysts are similar.

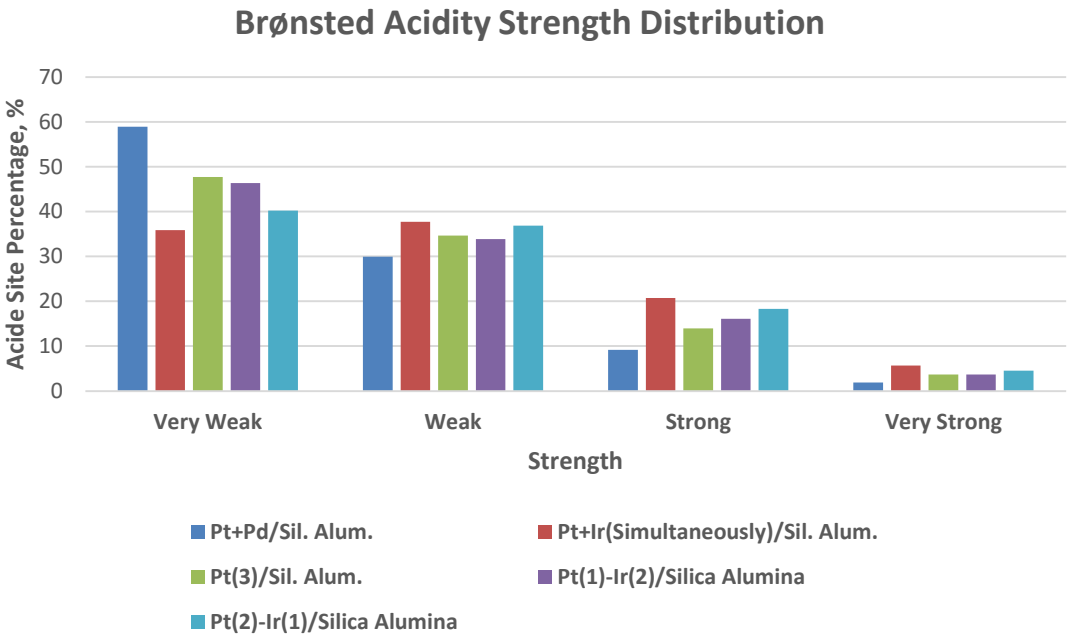


Figure 17: Distribution of the strength of Brønsted acid sites

4 Catalyst evaluation results

The catalysts were compared to each other in relation to conversion of feedstock (percentage of feedstock turned into product) and selectivity to examine their relative effectiveness in order to determine the one with the highest potential in hydroisomerization.

4.1 Catalyst comparison and evaluation in the hydroisomerization of n-hexadecane

Conversion alone is not enough to determine the performance of the catalyst since it only gives us information on how much of the feedstock was consumed but not on the quality of the product that may vary widely between catalysts and operating conditions.

The selectivity of the process towards hydrocarbons of long chain length and particularly isomers of the same size as the feedstock is very important. This is because the feedstock consumed needs to be converted into a product with upgraded characteristics in the range of diesel as opposed to being cracked.

Ultimately the effectiveness of the catalyst is determined by the yield of i-hexadecane in relation to the consumed feedstock. Furthermore, in selecting the catalyst with the highest potential in any given process, the relative cost of the catalyst, its stability and resistance to poisons has to be considered as well.

4.1.1 Conversion, selectivity and yield

The extent of the conversion of the feedstock to the different products is strongly influenced by the residence time of the reactants in the catalytic bed. Here the residence time is inversely represented by the value of Weight Hourly Space Velocity (WHSV), since the smaller the value of WHSV the longer the residence time is. In Figure 18 the significant effect of residence time is obvious.

The conversion ranges from 7% to 43% in the range of WHSV tested. It is significantly higher for lower WSHV (longer residence times) as there is more time for the reactions to take place and thus a much bigger percentage of the feedstock can be converted.

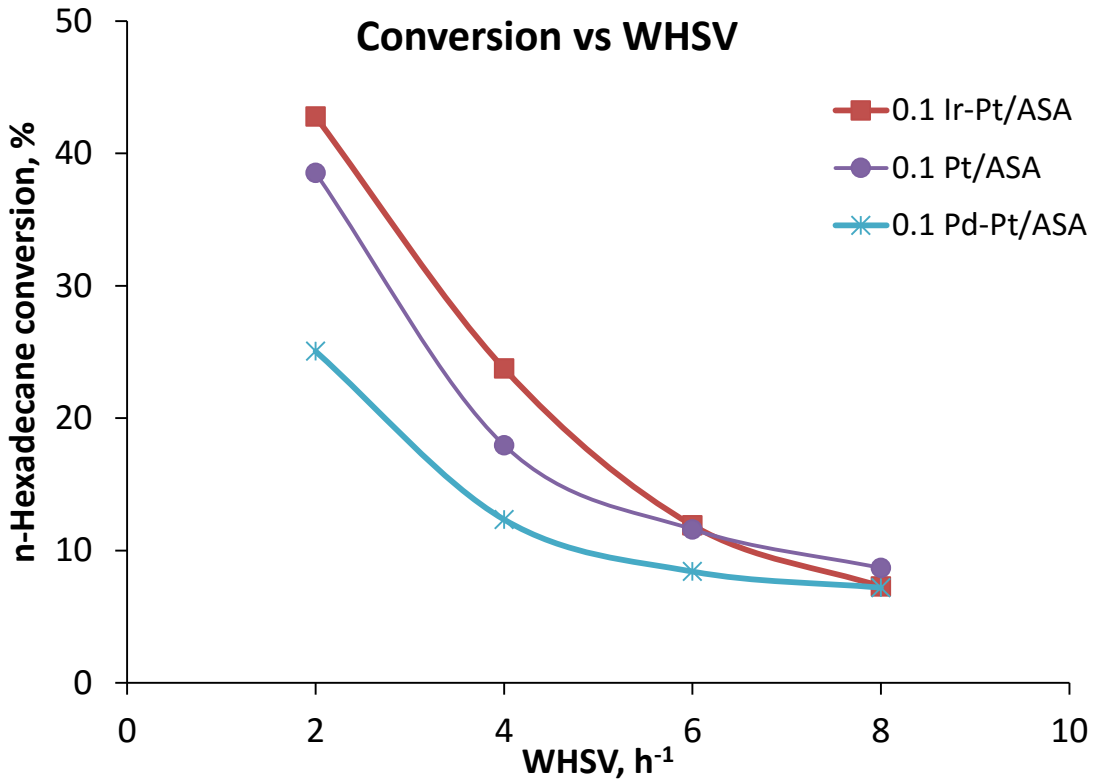


Figure 18: Feedstock conversion vs WHSV comparison for different catalysts

For higher WHSV the conversion of the feedstock is very low. Furthermore there is negligible difference between the different catalysts. Both facts can be attributed to the velocity of the stream which does not let pore diffusion act since the residence time is so low. In essence the feedstocks don't have enough time to enter the pore system of the catalytic particles as they are quickly swept away. This results in much less surface area being utilized, since most of it is actually provided by the pore walls. Even on the surface that is being utilized the residence time is not enough for the difference, in the characteristics of the catalysts to have a substantial effect as far as conversion is concerned.

On the contrary there is significant difference in the conversion of n-hexadecane, between the catalysts, for the lowest WHSV where residence time is much higher and the particularities of every catalyst can have a significant effect. The addition of Ir enhances conversion in contrast to Pd that significantly reduces it. The Pd-Pt catalyst is, by far, the worst in conversion and selectivity, as will be explained later.

The high conversion achieved by the Ir-Pt catalyst can be attributed to the metal sites of the Ir-Pt catalyst being significantly more active (by virtue of quality) because the high

hydrogenolysis potential [67]of Ir which might be enough to counter act the significantly lower surface area in comparison to the Pt catalyst. Comparing Figure 14 and Figure 12, we see that the acidities of the Ir-Pt and Pt catalysts are very similar despite of the difference in surface area and that Ir-Pt has more Brønsted acid sites, which are important to the activity [68] of the catalyst and have been found to promote hydrocracking [69] especially when the sites are strong.

Alternatively, the case may be that the activity of the sites is not significantly higher but the very long residence time nullifies the advantage of the significantly larger porosity/surface area of the Pt catalyst. Or it could be a combination of both, with the metal sites on Ir-Pt being more active and the residence time being just enough to counter act the difference in surface.

The combination of the above explanations seems to better fit the results. As can be seen in Figure 18 the conversion for Ir-Pt is initially lower than it is for Pt but surpasses it as the residence time increases. Thus it may be that Ir-Pt sites are indeed more active than those of Pt but conversion is initially held back due to the effect of low surface area and residence time.

The low conversion values achieved by the Pd-Pt catalyst are in line with the fact that it has the lowest surface area out of all the catalysts that were synthesized. The combination of Pd and Pt in bimetallic catalysts is known to make the material more resistant to poisons but due to the way atoms are arranged on the surface (described in paragraph 3.2) the hydrogenation activity of the catalyst suffers because Pt is less exposed due to it being covered to various extends by Pd atoms [70]. Thus less metal atoms are exposed and available to catalyse reactions.

In Figure 19 the selectivity to i-Hexadecane vs feedstock conversion is plotted and a significant difference, can be observed between the different catalysts as their selectivity ranges from 18% to 72%.

The selectivities of the different catalysts are very different for low conversions. Pure Pt seems to give the best results maintaining selectivities of more than 60% for conversions lower than 20%. The inclusion of Ir results in a drop to selectivities between 45 to 51 % and Pd reaches significantly lower values. For conversion values greater than 25% pure Pt and Ir-Pt have similar selectivities in the range of 30 to 40% while Pd-Pt does not reach such high conversions.

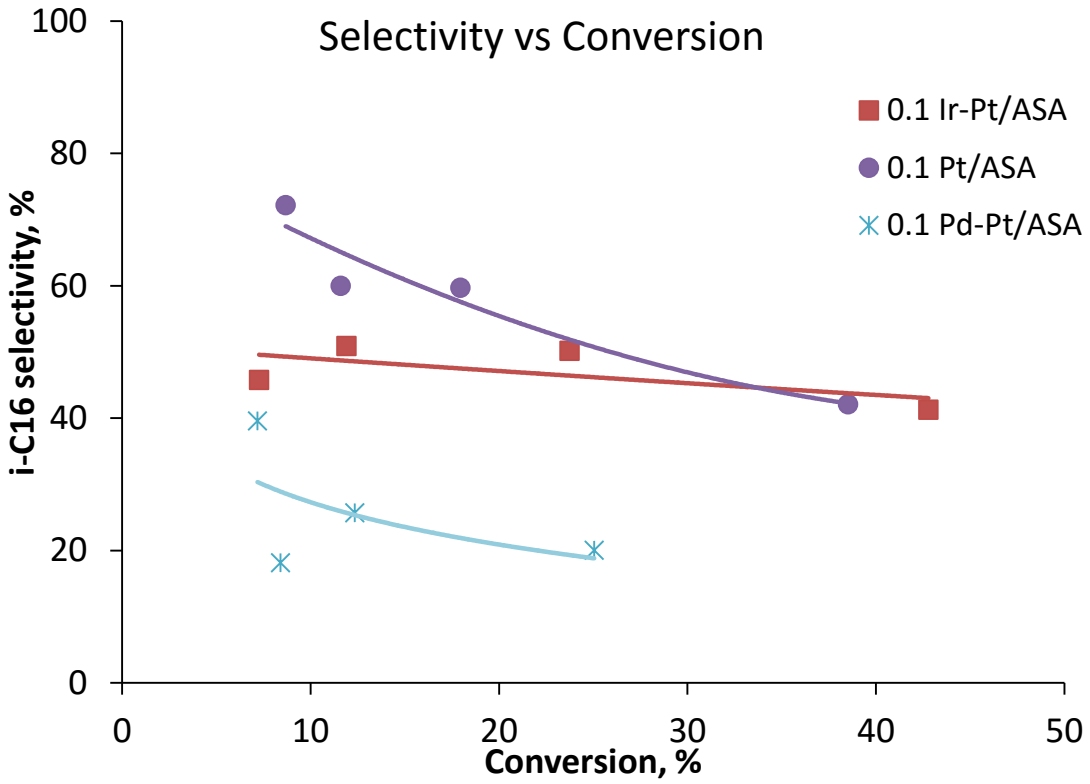


Figure 19: Selectivity to i-Hexadecane vs conversion comparison for different catalysts

Platinum is known for promoting hydroisomerization while as was mentioned before iridium promotes hydrogenolysis which leads to cracking. The result is that even though conversion is higher in the case of Ir-Pt catalyst, its selectivity is lower than that of Pt because of the activity of Ir.

In the case of the Pd-Pt catalyst the low selectivity can be attributed to the prominence of Pd on the surface (since much of the platinum is coved by palladium and unavailable) which has been shown [43] to promote hydrocracking.

Thus the choice of the particular metal, used to accompany platinum, is proven to a significant effect as between the two bimetallic catalysts, the Ir-Pt is much more selective than the Pd-Pt one and at least for low conversions, the inclusion of a second metal does not seem beneficial so far as selectivity is concerned. This may in part be caused by the greater concertation of metal atoms (regardless of type) on the surface of the two bimetallic catalysts (compared to the monometallic) which has been shown to have a negative effect [69] on the selectivity of the conversion of n-hexadecane.

From Figure 19, greater conversions seem to be accompanied by lower selectivities. This is in line with existing literature [43] [71] [65].The reason for this behaviour is that for lower conversions the product is composed mainly of, mono-branched, isomers of

the feedstock. These isomers are difficult to crack when compared to their multi-branched counterparts.

Thus for low residence times and low conversions the cracking product is limited. Apart from low residence time being accompanied by low conversion anyway, there are two ways in which hydrocracking is limited by these parameters.

In the case of low residence times, by the time mono- and multi-branched isomers are formed they are already leaving the catalytic bed and don't have the chance to undergo hydrocracking. In the case of low conversion, the concentration of isomers is low, so they are less likely to occupy an active site and be cracked.

As conversion increases, so does the generation of multi-branched isomers that are easier to crack and the cracking products increase exponentially and selectivity suffers until at 100% conversion all the feedstock is cracked. [65] [71]

As was mentioned before; in order to determine the most effective catalyst, conversion and selectivity, alone, are not enough. In Figure 20 the yield of i-Hexadecane can be seen plotted against selectivity.

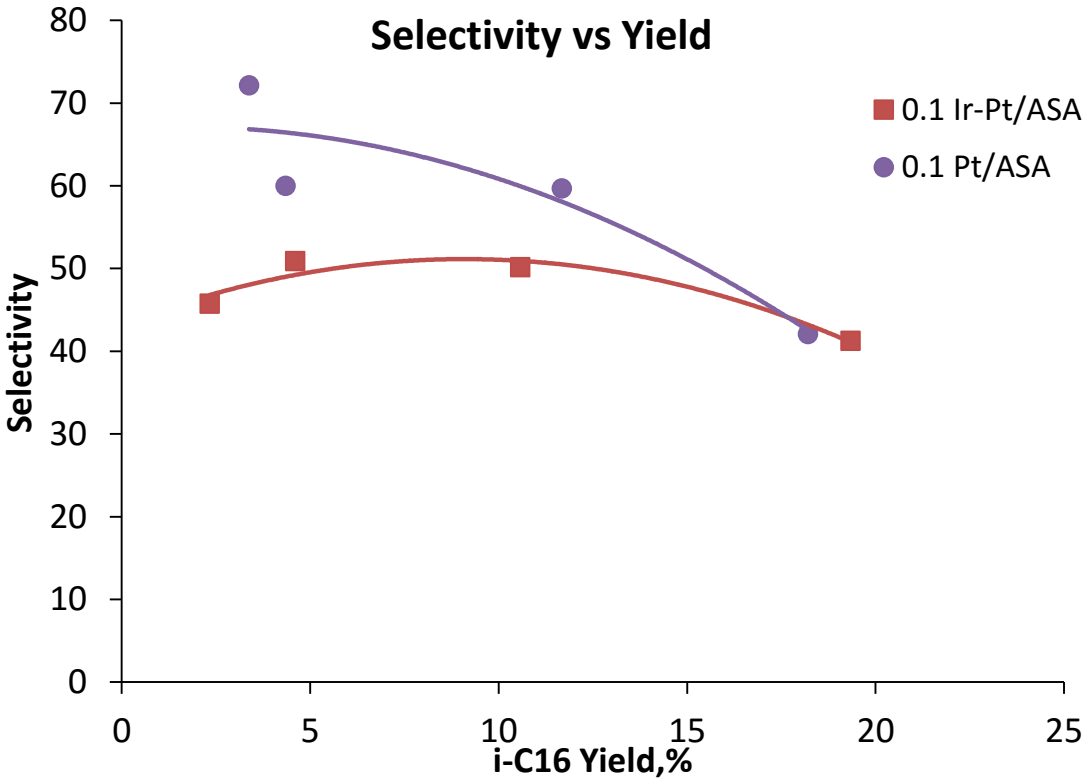


Figure 20: i-C16 yield versus selectivity

For yields higher than 17% Ir-Pt has better selectivity than Pt and consequently less feedstock is wasted due to hydrocracking. But for lower yields the Pt catalyst much more selective. Additionally both catalysts' selectivities drop as the yield is increased so the best utilization of the feedstock comes from Pt for low yields.

Smaller yield means greater investment cost for the same production capacity compared to larger yield but less waste and thus greater profit on the same feedstock. Whether the gains out weight the higher initial investment is subject to the particularities of each different project and are beyond the scope of this thesis.

As will be presented later, the formation of coke is much more severe in the case of Ir-Pt than in the case of Pt. Thus, for greater yields, deactivation due to coke formation will be a greater issue for Ir-Pt. Thus if the quality of the product and resistance to deactivation are important Pt is a better choice. Additionally for the monometallic Pt the cost of the catalyst would be much lower since Ir, which is expensive, is not used and the overall amount of precious metal is almost half in the case of the Pt catalyst.

Consequently it seems that the Pt catalyst is the most preferable choice since it offers better utilization of the feedstock, less problems due to coking and possibly an economically more viable process.

4.1.2 Effect of preparation sequence in Pt/Ir catalysts

We have seen that the second metal, used to impregnate the catalytic support has an effect on the effectiveness of the catalyst so, as was described before, in order to test the effect of order of impregnation two additional catalysts were synthesized. The additional catalysts where chosen to be variants of the Ir-Pt catalyst since it was proven to be the better of the two bimetallic catalysts in conversion and selectivity.

The new catalysts were tested under the same conditions as the three original ones and the conversion results can be seen in Figure 21, compared with the three original catalysts.

Conversion wise the original Ir-Pt catalyst where the Ir was added first, remains the most effective. The one that was impregnated first with Pt was more similar to the actual Pt catalyst for low to medium WHSV but with a conversion already too low for WHSV 6, it was not tested for WHSV 8, while the simultaneously impregnated catalyst gives results, very similar to that of the Pd-Pt catalyst.

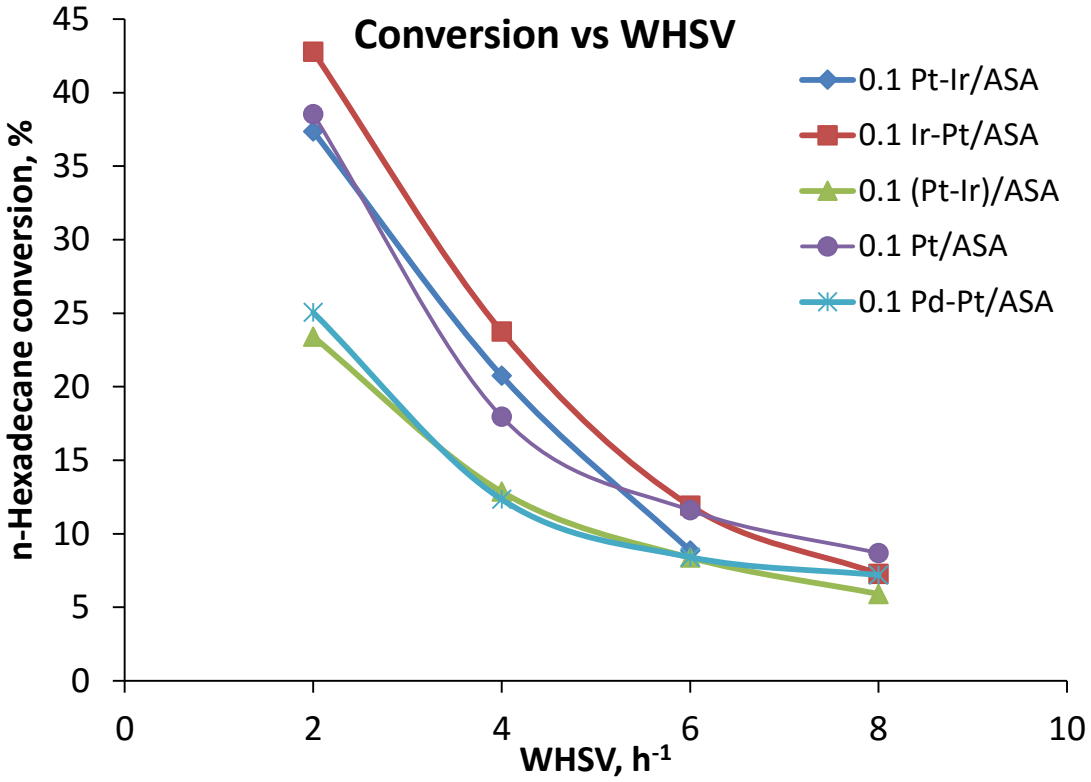


Figure 21: Conversion vs WHSV

The order of conversion follows the order of acidity of the three catalyst with Ir-Pt exhibiting the highest conversion and acidity while having the least available surface area of the three and (Pt-Ir) having the lowest conversion and acidity even though its surface area is significantly larger than the other two.

A possible explanation for this discrepancy may be the way that iridium atoms are dispersed on the surface of the catalyst. It has been observed [67] that the hydrogenolysis activity of iridium is affected by the size of the clusters it forms. Comparing the metal content results (Figure 13) with the conversion results for the three Ir variants we see that their order regarding the amount of detected platinum is in the same as their order in regard to the conversion values; namely Ir-Pt > Pt-Ir > (Pt-Ir).

As was described in paragraph 3.2 the reason for the apparent disappearance of part of the platinum from the catalysts is that it forms alloys with iridium that are not detected. Additionally it was described that the metal atoms form cluster of Pt, crystallites of Ir and bimetallic clusters where Pt is dominant.

Considering all the above the difference in activity may be attributed to the difference in the size and number of Ir crystallites. The greater the amount of alloy created the less iridium is available to create crystallites of the appropriate size and so its activity drops.

Thus the (Pt-Ir) catalyst that has appears to have the least amount of Pt also achieves much lower conversion than Ir-Pt which appears has the higher amount on Pt.

Even though, conversion wise, the Pd-Pt and (Pt-Ir) catalysts were very similar, the same does not hold selectivity wise, where there is a significant difference between the two catalysts. In Figure 22 the difference in selectivity is obvious as the (Pt-Ir) is almost 100% more selective probably due to the limited exposure of Pt as was described before and the hydrocracking activity of palladium.

The Pt-Ir catalyst is similar in selectivity to the Ir-Pt as is the case with conversion, although it is actually somewhat more selective for low conversion values.

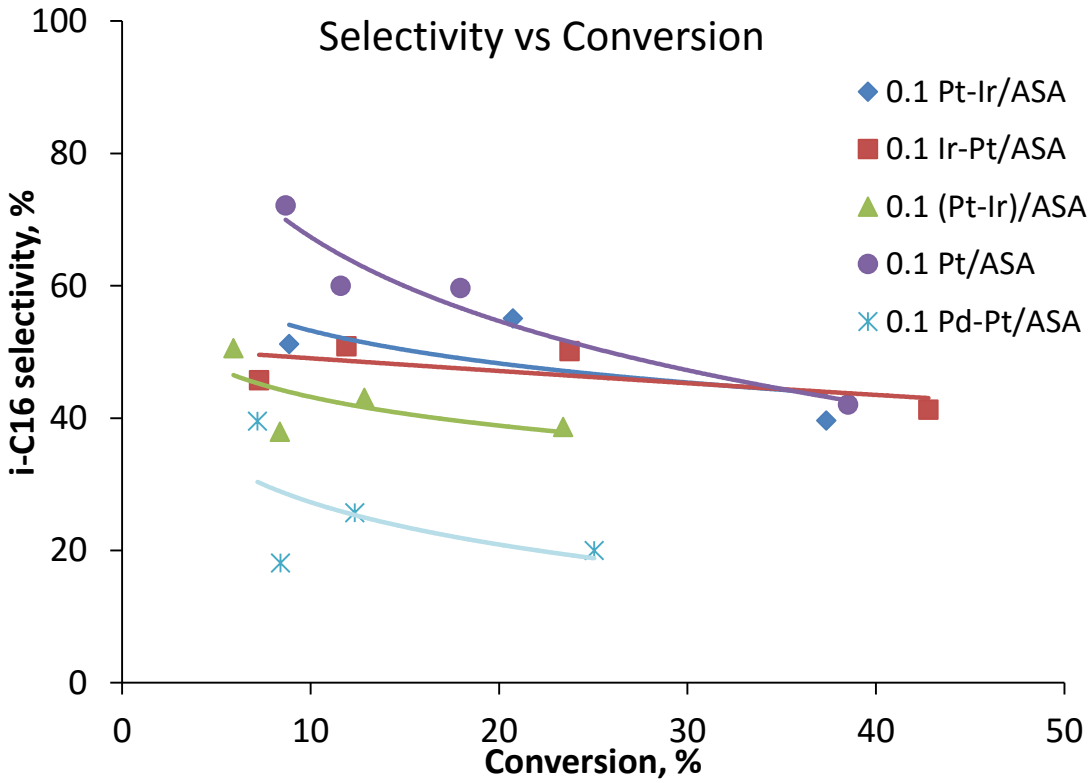


Figure 22: Selectivity to i-Hexadecane vs WHSV comparison for all the tested catalysts

By the end of the first set of experiments it was decided that, all things considered, Pt/Silica-Alumina was deemed to be the most appropriate catalyst for further study.

4.2 Evaluation on alternative feedstock

Before proceeding to testing the catalyst with the mixed feedstock, an intermediate experiment was conducted to evaluate the effect of the chain length of the feedstock molecules. For this reason the feedstock was changed to n-Heptadecane while catalyst and operating conditions remained the same.

At first glance there is not much difference between the two feedstocks. As Figure 23 shows conversion is slightly higher for C_{17} for all residence times which is to be expected as thermodynamically the longer chain will be more reactive. [72]

The picture does not change dramatically when comparing selectivities at low conversions, as Figure 24 shows; but as conversion gets higher there is significant deviation between the selectivities for the two different feedstocks, with the process being 35% more selective with the higher carbon number feedstock.

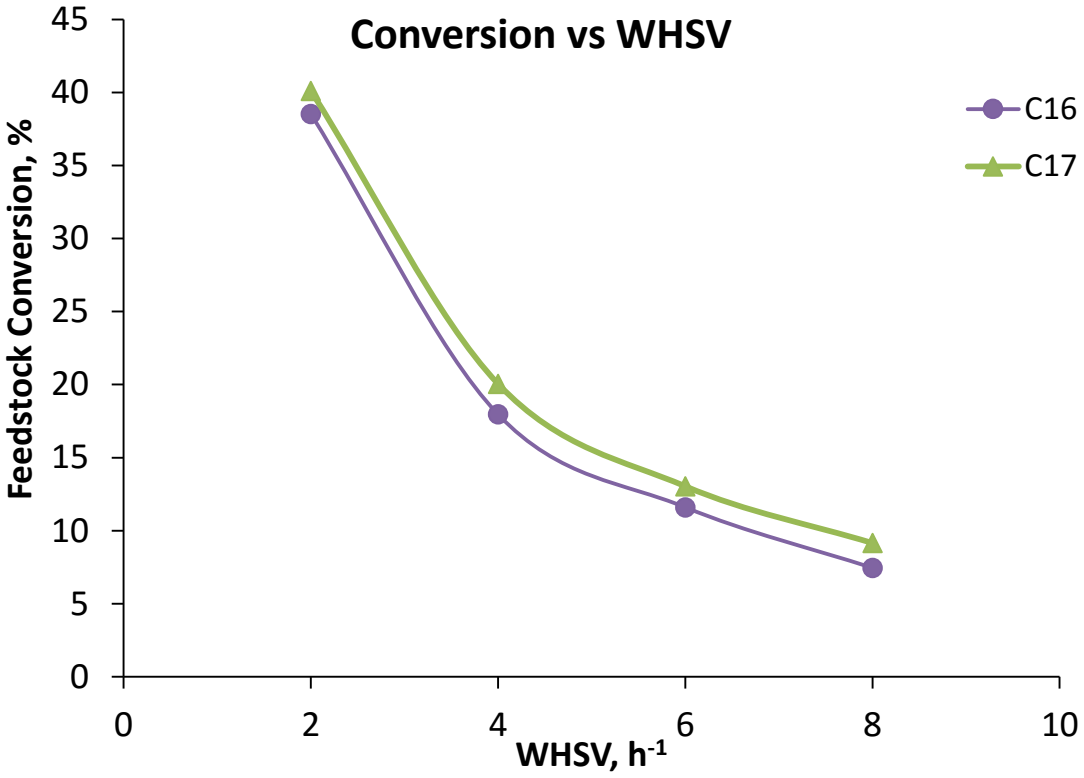


Figure 23: Conversion vs WHSV comparison between n-Heptadecane and n-Hexadecane

Once again the low residence time in the low conversion range does not seem to allow for the differences between the substances involved to manifest. In higher residence times where higher conversions are achieved, the cracking function seems to be more effective, especially in the case of the smaller molecule.

We see that the change of feedstock has a significant effect even though the change in chain length was the minimum possible. The increase of the chain length has been observed to lead to a reduction in selectivity when paraffins of significantly different chain length were compared [71].

This was not the case in this thesis results; this could be attributed to differences in the operating conditions metal loading and acid support. The particular pore structure of the

catalytic material may have been such that the slightly bigger mono- and multi-branched Heptadecane isomers were protected from further isomerization and cracking do to hindered entrance in the pores.

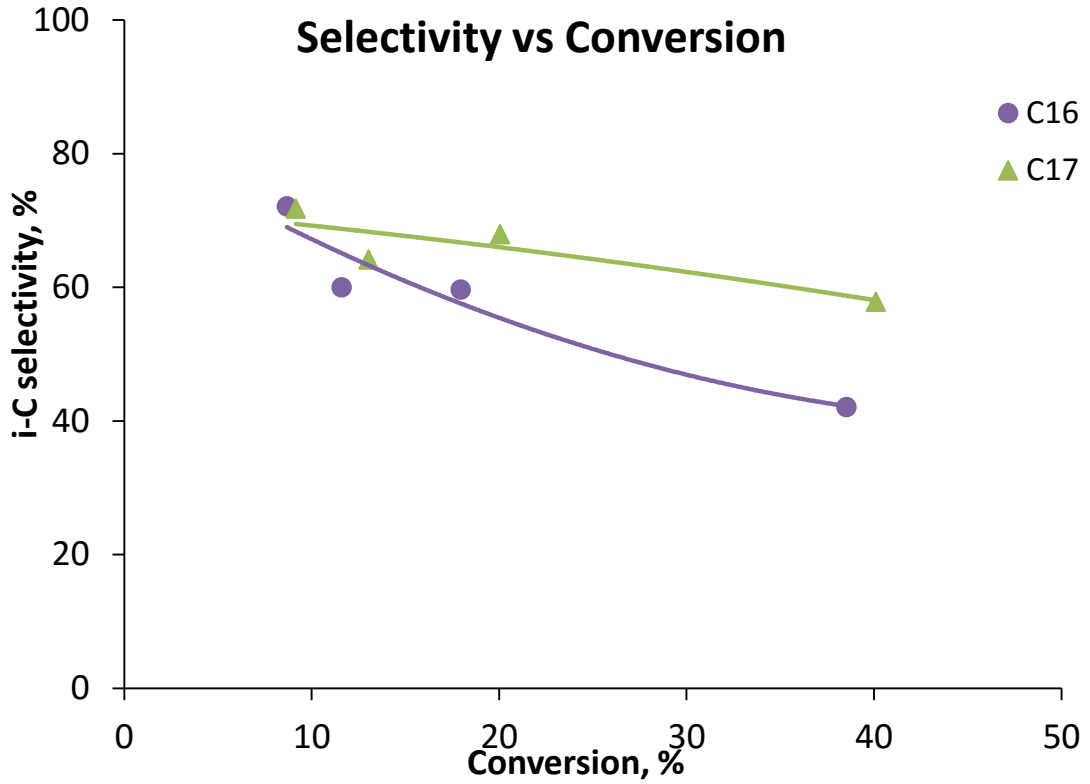


Figure 24: Selectivity vs conversion comparison between n-Heptadecane and n-Hexadecane

5 Hydroprocessing of diesel from VGO-castor oil mixture

After the choice of the most appropriate catalyst was made, the final experiment was conducted where the feedstock was the diesel fraction derived from hydrocracked mixture of VGO and castor oil. The fraction was representative of the feedstock that would be encountered in an industrial setting.

In the case of the VGO-castor oil diesel feedstock, the Pt/ASA catalyst was tested at 310°C and a WHSV of 6 h-1 at pressures of 20 bar and 40 bar.

The catalyst managed to significantly reduce the sulfur content of the feedstock the values of which are presented in Table 5. There was also a minor change in density. Changing to the higher pressure resulted in even greater reduction of the Sulphur content but on the contrary the reduction of the density was less than that of the lower pressure. Additionally the yield of the liquid and gaseous products was lower for the higher operating pressure.

Table 5: Comparison of Sulphur content and density

	Feedstock	**Product at 20 bar**	**Product at 40 bar**
Sulphur (ppm)	31.5	7.4	5.1
Density (g/ml)	0.869	0.863	0.859
Pour point (°C)	-9	-12	-12
Liquid yield (wt% on feed)	-	96.95	94.28
Gas yield (wt% on feed)	-	1.27	0.64

Regardless of the pressure, the process achieved a product with a better the pour point than that of the feedstock that was reduced from -9°C to -12°C. Nevertheless some cracking was not avoided and as is shown in Table 6 there was a small reduction of the percentage of diesel range hydrocarbons in favor of gasoline and residue range ones.

The extent, was however very low in both pressures studied, indicating that no significant cracking takes place under the investigated experimental conditions.

Table 6: Hydrocarbon chain length distribution (SimDis results)

Chain length	Feedstock	Product at 20 bar	Product at 40 bar
Gasoline range	0.8	3.4	3.8
Diesel range	95.8	91	91.1
Residue range	3.4	5.6	5.0

Table 7 presents a more detailed distribution of the hydrocarbon species that comprise the feedstock as well as the upgraded products determined by GCxGC analysis. The qualitative results obtained by GCxGC show that although a large reduction in the concentration of n-paraffins is achieved over the Pt/ASA catalyst, the content of iso-paraffins slightly decreases in the liquid product. Therefore we do not see a significant isomerization activity. However, the amount of the naphthenes and aromatics considerably increases, indicating that at the operating conditions employed with the specific feed and the catalytic material used, the main reactions that take place are the cyclization of the n-paraffins to naphthenes and the subsequent dehydrogenation of part of these naphthenes to aromatics. In terms of cold flow properties, although isomerization was not observed, the pour point of the liquid products improves compared to that of the feed, probably due to the formation of aromatics.

Table 7: Hydrocarbon species distribution

Chain length	Feedstock	Product at 20 bar	Product at 40 bar
Normal Paraffins	60.07	38.69	36.02
Iso Paraffins	17.25	13.31	12.31
Saturated Naphthenes	6.06	18.57	23.96
Normal Olefins	1.83	1.15	3.18
Aromatics	9.28	18.57	16.89
Unsaturated Naphthenes	2.47	4.66	5.45
Iso Olefins	0.62	2.04	1.31
Oxygenates	0	1.32	0.16
Nitrogen	0	0.27	0.4

6 Post-reaction catalyst characterization

6.1 Coke

Coke, which forms on the catalytic surface during hydroprocessing, causes the deactivation of the catalyst and is a major consideration in the planning of any hydroprocessing project. Thus there has been a lot of research [73], around understanding and preventing its formation.

Table 8 presents the amount of coke deposited on the catalysts expressed as μg of carbon per g of catalyst and g of feedstock and the hydrogen to carbon ratio in the coke. Comparing the coke results between the n-hexadecane and n-heptadecane feedstocks for the platinum catalyst we see that the formation of coke is higher for the n-hexadecane even though conversion was somewhat lower compared to n-heptadecane. This could be attributed to the lower selectivity achieved with the n-hexadecane feedstock which means more cracking and more coke formation. In general, the extent of coking on the monometallic Pt/ASA catalyst is low, regardless of the feedstock. This can be attributed to the high dispersion of Pt atoms on the surface of the catalyst which has been found [74] to suppress coke formation.

In the case of the diesel feedstock an additional possible explanation could be the higher pressure that the catalyst was subjected to. Higher hydrogen pressure [73] favor hydrogenation of the coke precursor molecules before they have the chance to polymerize and form coke.

The low coke formation of the Pd-Pt catalyst could be attributed to both the low conversion achieved as well as the ability of Pd to provide resistance to poisons.

The results of the elemental analysis show that the hydrogen to carbon ratio ranges from 1.06 to 2.26. This hints to the existence of relatively easy to combust coke that has not been graphitized yet since there is still a significant amount of hydrogen compared to the ratios that would signify the dominance of polyaromatic and more graphite like compounds.

Table 8: Coke formation on the used catalysts

Catalyst	Feedstock	Carbon retention (μgC/(gCatalyst*gFeedstock))	Hydrogen to carbon molar ratio
Pt-Ir/ASA	C16	625	1.17
Ir-Pt/ ASA	C16	525	1.06
(Pt-Ir)/ ASA	C16	390	1.2
Pt/ ASA	C16	270	1.16
Pd-Pt/ ASA	C16	242	1.29
Pt/ ASA	C17	213	1.56
Pt/ ASA	Castor-oil/VGO	126	2.26

6.2 Temperature Programmed Oxidation

The used catalysts were subjected to temperature programmed oxidation in a thermogravimetric analyzer to obtain information on the nature of the coke deposits and their ease of removal. Figures Figure 25 through Figure 27 show the derivative of the weight loss as a function of temperature for all catalysts. The first peak is located at around 50-65°C and possibly corresponds to removal of moisture from the surface as the temperature starts increasing. The second and most prominent peak occurs at around 199-210°C and represents the majority of the coke species on the surface. A third minor peak can be observed between 240-260°C, while a high temperature peak is also apparent at 510-565°C.

The first and fourth, peaks appear with similar intensity and width in almost all catalysts. Exceptions, are Pt-Ir/ASA for the fourth peak and Ir-Pt for the first peak. The same is not true for the other two. The second peak appears in all but the final case where the diesel derived from the Castor-oil/VGO mixture is used as feedstock, possibly for the reason described in paragraph 6.1.

Lastly the third peak appears in varying intensities or does not appear at all. The peak appears in its greatest intensity in the Pd-Pt catalyst. It is less intense in the Pt catalysts, used with model compounds, irrespective of the feedstock (n-hexadecane/n-heptadecane) but does not appear at all in the case of the diesel while it is barely visible in the case of the Ir/Pt variants.

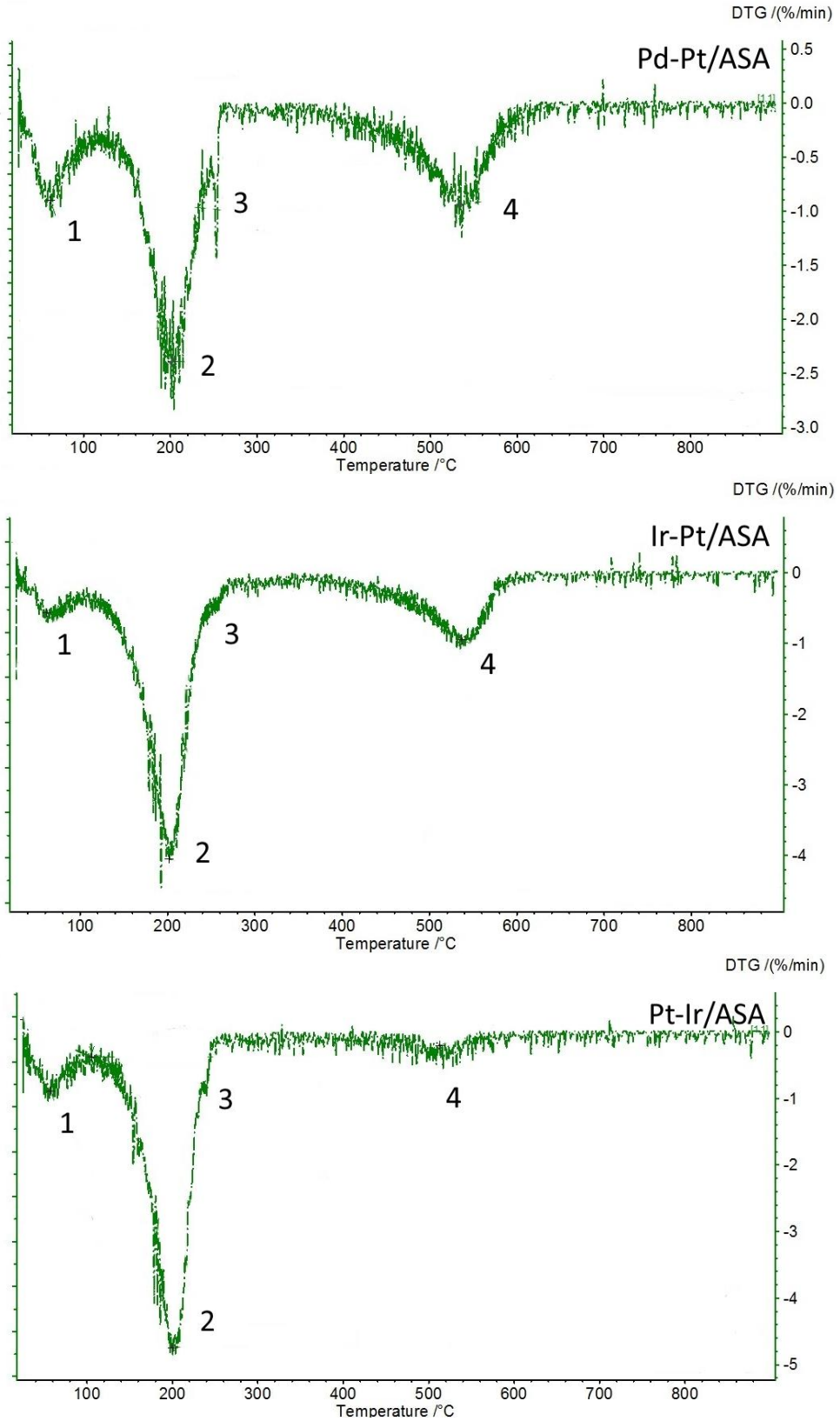


Figure 25: TPO profiles of Pd-Pt, Ir-Pt and Pt-Ir /ASA

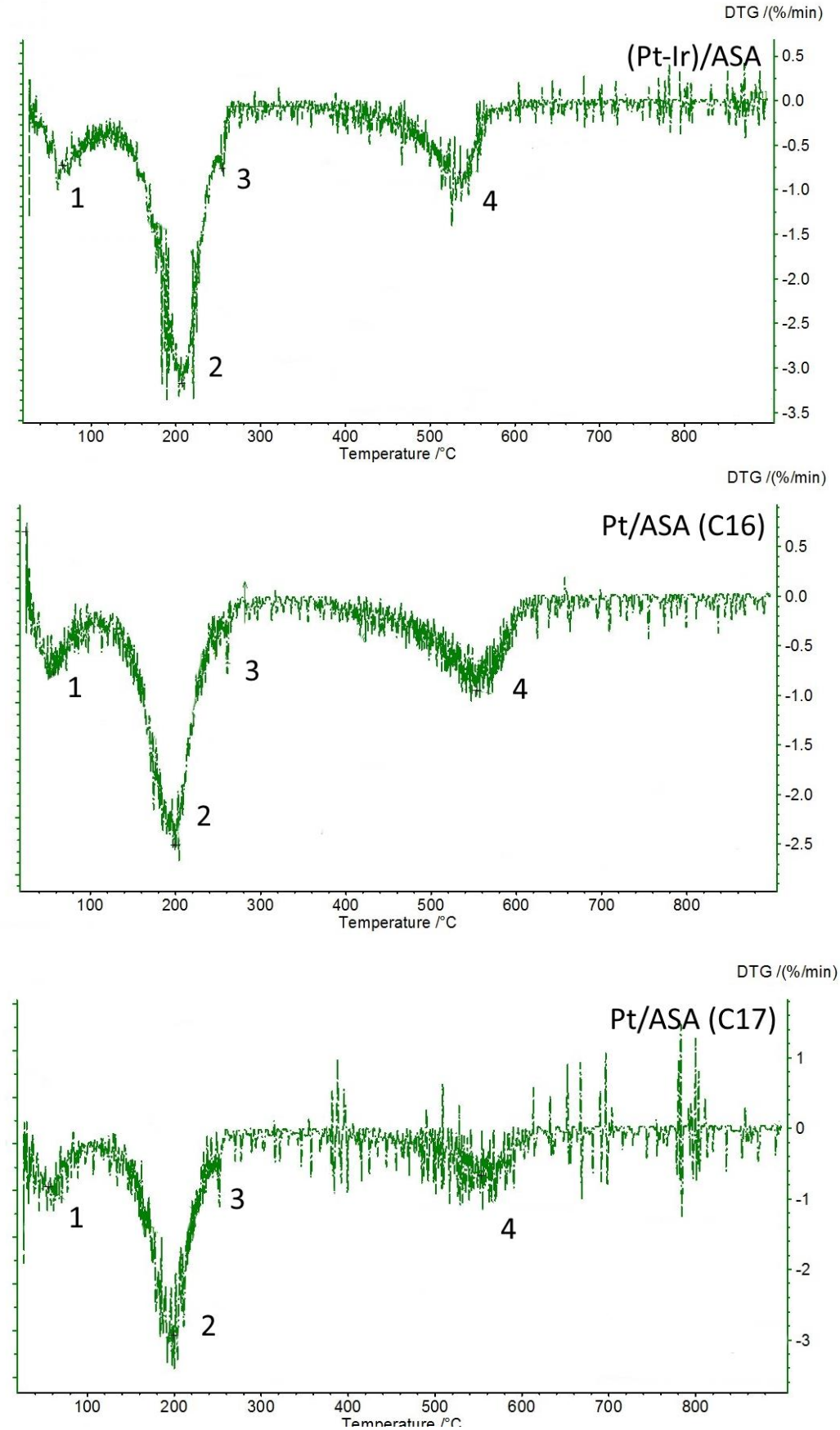


Figure 26: TPO profiles of (Pt-Ir), Pt C16 and Pt C17 /ASA

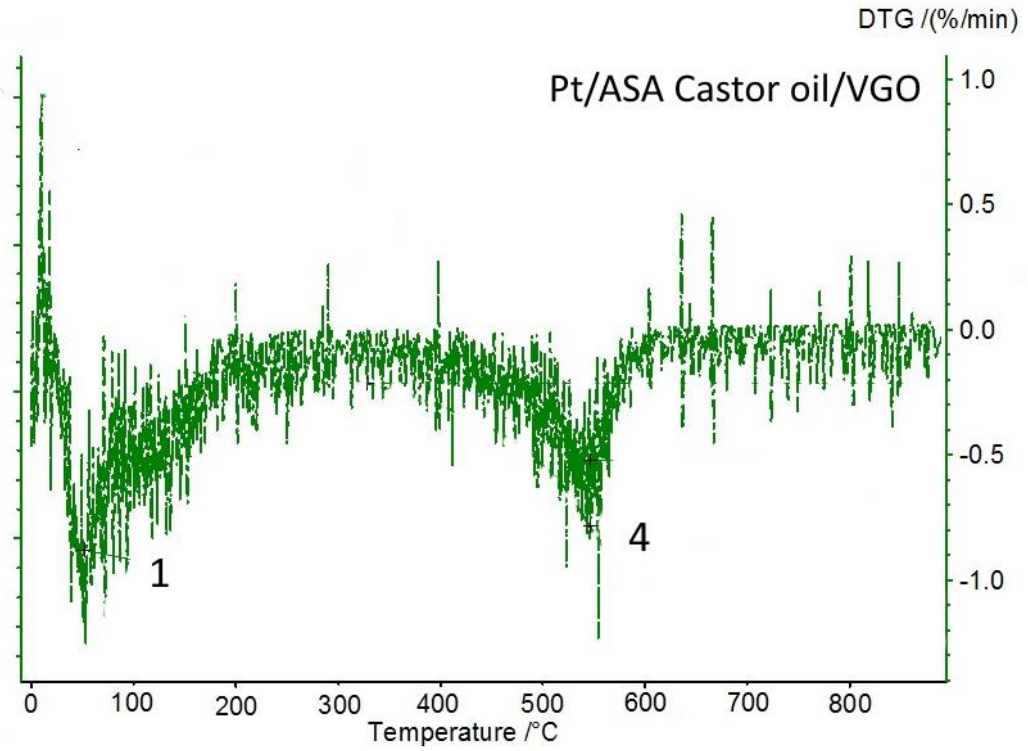


Figure 27: TPO profile of Pt/ASA Castor oil/VGO

The small peak at low temperatures has been associated in other studies with physisorbed water molecules and volatile compounds [75].

The second peak could be attributed to the combustion of poorly polymerized coke located on or near the metal sites. The fourth peak has been found [65] [76] to correspond to the highly polymerized coke that is graphite like. This kind of coke forms on the acid sites of the support.

The third peak has been found to correspond to coke that forms on atoms of high coordination number in a study on palladium catalysts [76] which is in line with the increased intensity of the peak for the Pd-Pt catalyst.

Table 9 presents a comparison of the results of elemental analysis against mass change from TPO. Differentiation can be observed between the results of the two methods. The difference between them is also presented and seems to follow the same order as coke formation with the exception of Ir-Pt which exhibits the greatest difference but the second larger coke formation.

Table 9: Comparison of elemental and TPO analysis

Catalyst	Elemental C+H,%	Difference	TPO weight loss,%
Ir-Pt/ASA	52.31	14.05	38.26
Pt-Ir/ASA	50.14	12.41	37.73
(Pt-Ir)/ASA	40.18	7.81	32.37
Pt/ASA	32.99	3.6	29.39
Pd-Pt/ASA	32.07	0.51	31.56
Pt/ASA (C17)	27.28	-3.92	31.2
Pt/ASA (Castor/VGO)	8.09	-10.46	18.55

7 Conclusions

A series of mono and bimetallic bifunctional catalysts where synthesized combining platinum (Pt), palladium (Pd) and iridium (Ir) on commercial amorphous silica alumina (ASA) support. Five catalysts were synthesized; one monometallic and four bimetallic. All catalysts were made by depositing metal atoms on the support via the dry impregnation method.

The combinations synthesized where Pt/ASA, Pd-Pt/ASA, and three Ir/Pt variants (Ir-Pt,(Pt-Ir),Pt-Ir) in order to investigate the effect of the order of impregnation on the performance and characteristics of the catalysts.

Before being tested to evaluate their potential, the catalysts were characterized to gain insight on their properties and their effect on hydroprocessing activity.

The catalytic surface area was found to differ greatly between catalysts. This was probably caused by sintering during the calcination process while it is possible that the addition of metal atoms that form clusters and crystallites may have in part led to clogging of pores.

The impregnation order was found to have a significant effect on the properties of the catalysts by affecting the distribution and composition of the metal sites on the surface of the catalysts which have an impact on the performance of the catalyst during operation. The order of impregnation of Ir and Pt has led to differing levels of alloy formation between the two kinds of metal that has a significant effect on their hydroprocessing ability because it affects the dispersion of metal sites and the size of iridium crystallites.

Acidity of the support of catalysts is connected to their hydroprocessing performance. The support used in this thesis was found to have a majority of mostly strong Lewis acid sites and a smaller amount of Brønsted acid sites the population of which is enhanced by the addition of platinum.

The Brønsted acids sites are, in their majority, of mild strength which is thought to promote hydroisomerization while most of the Lewis sites are very strong and promote hydrocracking. As expected the acidity of the catalyst grows along with available surface area as the acid sites are provided by the support. The monometallic platinum is a nota-

ble exception as even though it has a large surface area its acidity is lower than most of the other catalyst which might be explained by the observed ability of platinum to suppress overall acidity on bifunctional catalysts.

While testing the catalysts in the hydroprocessing of n-hexadecane it is obvious that residence time plays a pivotal role in the conversion of feedstock in part by affecting the ease of entrance to the pores. The selectivity was also strongly affected by the ability of Pt atoms to interact with the reactants.

Taking various consideration into account it was decided that monometallic platinum was the best catalyst to be used under more demanding conditions.

When we attempted to evaluate the effect of feedstock chain length on the performance of the catalyst led it was fund that longer chain length results in more conversion and better selectivity probably due to the effect of the interplay between pore structure and the size of the reacting molecules.

Hydroprocessing VGO/Castor oil diesel feedstock using the Pt/ASA catalyst led to an upgrade of the quality of the product resulting in lower Sulphur content and a better pour point while no significant cracking was observed.

Coke formation on the catalysts was found to be affected by the distribution of the metal atoms on the surface of the catalyst is suppressed by the presence of highly dispersed platinum.

The coke forming on the catalysts have been found to correspond to three different kinds. An easily combusted on that forms on or near metal sites and is responsible for most of the coke mass, a minor one that has been found in other studies to correspond to atoms of high coordination number and lastly a much more difficult to crack graphite like coke.

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